JUN 10 1926

VOLUME 27 SECOND SERIES NUMBER 6

THE PHYSICAL REVIEW

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A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

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THE PHYSICAL REVIEW

Published monthly

Two volumes annually

First series. From July 1, 1893 to January 1, 1913, the Review was conducted by Edward L. Nichols, Ernest Merrit and Frederick Bedell, with the financial support of Cornell University. The first four volumes were issued annually; subsequent volumes, semi-annually; thirty-five volumes in all.

Second series. On January 1, 1913, the Review was transferred to the American Physical Society as announced on the first page of the new series which was then begun. Since then it has been conducted by a Board of Editors elected by the Society. Semi-annual volumes begin in January and July.

Contributors are referred to page 2 of the advertisements for further information.

Annual Subscription, throughout the Postal Union, $7.00 in advance.

Single Copies, $.75.

General Index, 1893-1920, $4.00, in advance.

Back Volumes, $4.50 per volume; Back Numbers, $.75 per copy. Postage is free if remittance accompanies order; otherwise postage is extra. No bound volumes can be supplied. The Review offers to purchase a limited number of First Series, Vol. 1, No. 1 (at $1.50 each); Second Series, Vol. 7, No. 1, January 1916; Vol. 7, February 1916 and Vol. 9, No. 2, February 1917 (at $1.50 each); Vol. 19, No. 1, January 1922 (at $.75 each).

Advertisements. Rates will be supplied by the Editor on request. Copy for each number must be received at Corning before the 1st of the preceding month; old copy is used until new copy is received. Send electrotypes direct to the printers, George Banta Publishing Co., Menasha, Wisconsin.

Discount of ten per cent is allowed subscription agencies and members of the American Physical Society.

Complaints of failure to receive the Review, in the case of members of the Physical Society, should be addressed to the Treasurer; otherwise, to the Editor. *New copies will be sent free only if complaint is received within three months of date of issue.*

Correspondence should be addressed to the Physical Review, 1500 University Ave. S. E., Minneapolis, Minn.

Entered at the postoffice at Menasha, Wis., as second class matter.
Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized September 6, 1922.

Second Series *June, 1926* *Vol. 27, No. 6*

THE

PHYSICAL REVIEW

HIGH FREQUENCY RAYS OF COSMIC ORIGIN
II. MOUNTAIN PEAK AND AIRPLANE OBSERVATIONS

By R. A. Millikan and R. M. Otis

Abstract

The elimination in penetrating ray experiments of temperature and pressure effects is accomplished through *new features in the design of Wulf electroscopes*, but especially through immediate reduction in situ of all deflections to volts.

Variation of penetrating radiation with altitude and with time of day.—When suitable precautions are taken for eliminating the activity of adjacent rocks, both airplane and mountain peak observations agree in showing a definite variation of the penetrating radiation with altitude alone. Within the limits of experimental error all observations are consistent in showing no dependence of the penetrating radiation upon the time of day or upon the position of heavenly bodies.

Absorption coefficients of penetrating rays.—Absorption experiments made on Pikes Peak with lead sheets 4.8 cm thick furnish evidence for the existence on mountain peaks of copious new rays of local origin of no greater hardness than that of gamma rays. If these new rays are assumed to be homogeneous their absorption coefficient is about 3.1 per meter of water. These experiments, however, furnish no definite evidence for the existence of very penetrating rays of cosmic origin.

Necessary characteristics of cosmic rays if they exist—Such rays cannot produce as much as 2 ions per cc per sec. at sea level if they have an absorption coefficient not less than 0.25 per meter of water. If cosmic rays exist at all they must be less intense than this, or else they must be more penetrating than anyone has as yet suggested.

I. Introduction

THE sounding balloon experiments reported in Part I[1] had shown that the integrated natural leak of electroscopes at altitudes up to 15.5 km was slightly larger than the leak at the surface covering the same time interval. They had, however, shown nothing about the distribution of the leak with altitude, and they had shown nothing about the hardness of the rays causing the leak, further than to prove that if there were any rays of cosmic origin they must be very much more penetrating than had thus far been imagined in order to account for the smallness of the observed ionization. If, on the other hand, the

[1] Millikan and Bowen, Phys. Rev. **27**, 353 (1926).

small observed increase in ionization were due to radioactive materials in the atmosphere the penetrating rays should have the absorption coefficients of ordinary gamma rays.

In order to supply information upon these points a new group of experiments was planned and carried out in the summers of 1922–23. These involved (1) absorption experiments at the highest altitude to which we could transport considerable quantities of absorbing materials, and (2) experiments without absorbing screens in balloons, airplanes, and on mountain peaks to see whether altitude as such were a determining factor in the observed variations in the discharge rates, or whether there might be largely different discharge rates in different localities, thus accounting for the widely different results reported by different observers.

Suspecting, however, that these differences were due primarily to the failure to take suitable precautions against the influence of temperature upon the dimensions and elastic constants of the electroscopes, we adopted especial precautions for eliminating completely all such effects.

II. The Electroscope

The electroscope used is diagrammatically shown in Fig. 1 and a photograph of it inside a lead sheathing is reproduced in Fig. 3. This electroscope, which is of the Wulf type, was designed and constructed in the shops of the Norman Bridge Laboratory of Physics. Two quartz fibres of about 0.005 mm to 0.01 mm diameter and about 6 cm long, sputtered with platinum to make them conducting, are at the top soldered together into a small copper tube which is held by a set-screw in a brass cap, A, cemented to a long rod of quartz insulation. At their lower ends the fibres are fastened by a bead of shellac to a bow of unsputtered quartz fibre of slightly greater diameter. The ends of the bow are attached to brass pieces, B, whose effective lengths are adjustable, so that the fibres can be brought to the most efficient tension. This tension is one that will allow full-scale deflection when the electroscope is charged to the desired potential, but is still sufficient to make stable the fibres and to bring them together when uncharged. The screws for adjusting the tension on the fibres pass through an invar bridge which is supported in invar rods, C, which are in turn hung from approximately the same point in the top that supports the quartz insulator. Thus the tension is not changed by any deflection of the electroscope case due to a difference in pressure between the inside and the outside. Furthermore, inasmuch as the invar used was tested and ound to have a temperature coefficient of expansion practically equal

to that of quartz, the tension of the fibres should be independent of temperature also. This was found to be the case.

The case of the electroscope was made from cylindrical brass tubing, 1.7 mm to 1.8 mm thick. The bottom was of brass, 5 mm thick, while the top was of rolled zinc and most of the metal parts connected with the top were turned from zinc castings. This case was air-tight under a pressure of 60 lbs. per square inch above atmospheric pressure. The enclosed air was kept dry by phosphorus pentoxide which filled the

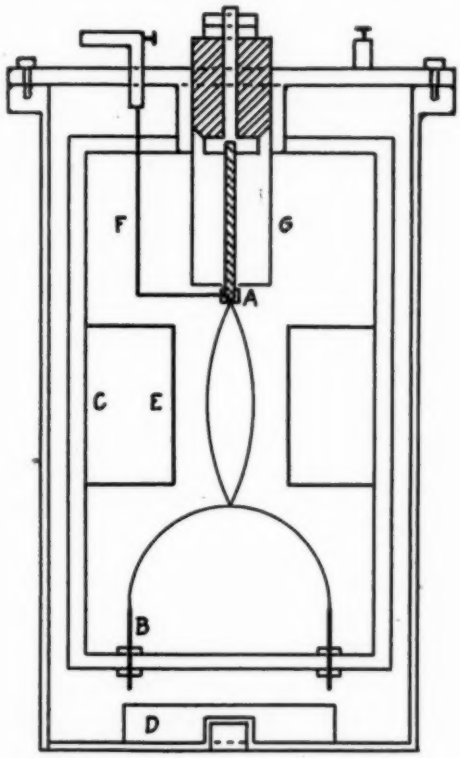


Fig. 1

flat cylindrical box, *D*, at the bottom of the electroscope. This box, which is covered by a perforated top to keep the phosphorus pentoxide from being shaken out where it might cause trouble, screws onto a lug projecting from the bottom of the case.

The positions of the fibres were determined with the aid of a microscope having a scale in the eyepiece. A window on the opposite side of the case provided light. Sunlight was used when possible; in other cases a small flash-light bulb attached to a projection over the window

was employed. The position of the objective as well as the eyepiece of the microscope could be varied, for the whole microscope fits into a tube, see Fig. 3, which extends into the case of the electroscope and terminates in a small glass window. This arrangement is very convenient because it is possible by simply removing the microscope to lower the electroscope into deep water without any protection and without fear of a leak. The fibres are kept in the focal plane of the microscope by the strengthened field due to the bent aluminum wires, E, projecting from the supporting invar rods. A very thick soft rubber gasket separates the top of the electroscope from the sides, so that the fibres could easily be swung into the center of the field of view by tightening the proper screws in the top.

The outside electrical connection to the fibres is made through the charging rod, F, which in the "on" position touches the brass cap to which the fibres are attached, and in the "off" position touches the case. This charging rod, as it passes through the case, is tapered at a very small angle to fit a greased ebonite bearing and is held tightly into contact by a strong spring.

A feature of the electroscope is that it is possible entirely to eliminate insulation loss if the loss across the thin quartz bow be neglected, and this is permissible because of the negligibly small diameter of the bow compared with the upper insulator. The quartz insulator is held in a brass rod which passes through an ebonite plug to the outside of the electroscope. This brass rod was held at the mean potential of the fibres throughout the period of observation thereby making impossible any insulation loss to the case. The brass rod and the quartz insulator are shielded from the rest of the electroscope by the shield, G, which is made in two parts, one of which may be rotated with respect to the other, leaving an opening to facilitate cleaning the insulator. The fact that the electroscope was designed with a view to accommodating lead screens accounts for the absence of projections from it and also for its small size. The volume was 1893 cc. The sensitivity varied in the different experiments from 1.4 to 2.1 volts per scale division. The capacity of the insulated system was found to be 1.32 cm.

III. Method of Observation

Essentially what is done in making a measurement of the penetrating radiation is to charge the electroscope to a known potential and note the drop in potential of the insulated fibres in a given interval of time. Then from these data and the known capacity of the fibres together with the volume, V, of enclosed air in the electroscope, and the

charge, e, on an electron, the rate of production of ions per unit volume can be calculated. Thus, the number of pairs of ions per cc per second which are formed is $C_f \Delta P/3600Ve$, where ΔP is the drop in potential of the fibres per hour.

However, the simple difference in the positions of the fibres as read on the scale is not an accurate measure of the potential drop of the fibres, especially after transportation of the electroscope from one place to another. Therefore, inasmuch as the electroscope was necessarily subjected to rather severe treatment, in order to destroy all doubt as to the meanings of the readings, the electroscope was calibrated before and after every period of observation, i.e., *the electroscope deflections were always reduced to volts at once and in situ.* This was easily and accurately accomplished by charging the electroscope to four known potentials in the region in which lay the reading to be interpreted. The four points thus obtained were plotted and a straight line was drawn through them. The four points almost always lay quite close to the line and it was never possible to make any large error. Such calibration at the time of reading is very essential to accurate results, for it was found that, while the sensitivity might not change appreciably, the whole calibration curve might from time to time move to the side, thereby changing the meaning in volts of a given deflection of the fibres. Also a slight change in focusing the microscope on the fibres of course changes the volt-value of the scale. These possibilities of error were completely eliminated by the method employed in these investigations.

The diagram of connections is shown in Fig. 2. When the switch S is in position 1, the battery is connected to the charging rod and to the case; when it is in position 2, it is connected to the guard ring on the quartz insulation and to the case. The 40,000 ohms resistance, R, is inserted in the electroscope circuit to avoid destructive currents if the charging rod should accidentally be brought into contact with the case while the switch S is still in position 1. Because no current flows through the electroscope, this resistance does not interfere with the measurement of potential.

The procedure in making an observation, then, is as follows: The charging rod is in the neutral position. The switch S is closed to position 1. The voltmeter switch is closed, a suitable potential is found on the battery, and the charging rod is connected to the fibres. The deflection of the fibres and the corresponding volts are then read as nearly simultaneously as possible. The charging rod is removed to neutral and a potential about 4 volts lower is found. The fibres are again charged and the deflection and volts are read. This is repeated

until four comparisons between deflection and volts have been obtained. The fibres are then charged to a potential lying in the midst of the four potentials previously applied, the charging rod is brought to neutral, the switch S is lifted to the neutral position, and the charging rod is turned so that it touches the case. The deflection and the time are then observed. This deflection is afterward interpreted in terms of volts and gives the potential at the beginning of the period of observation. The potential is now adjusted to equal the mean value of the potential of the fibres to be expected during the period of observation, the voltmeter switch is opened, and the switch S is closed to position 2, thereby putting this potential on the guard ring at the top of the quartz insulator and making impossible insulation loss. This potential need not be adjusted accurately, because the

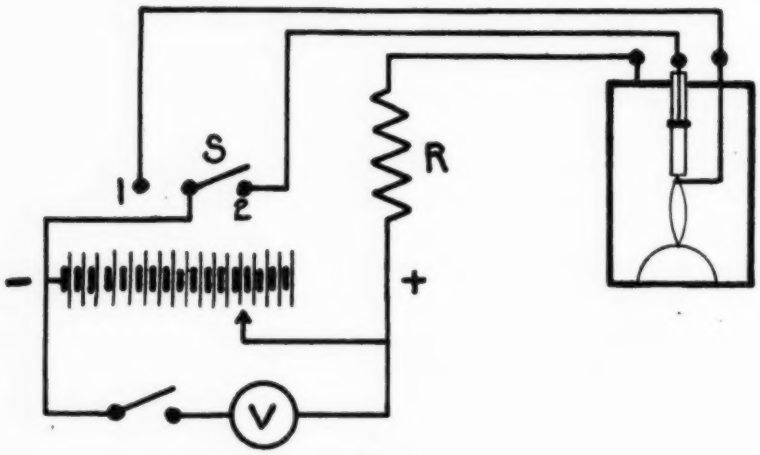


Fig. 2

insulation loss is probably negligibly small anyway. The guard ring was used only to make it impossible to criticize the results from the standpoint of insulation loss. At the end of the period of observation, the switch S is lifted to the neutral position, and the deflection of the fibres and the time are noted. The charging rod is turned to neutral and the process of calibration described above is gone through in order that the deflection just observed may be interpreted in volts. Suitable precautions were of course taken to insure saturation at all times and to permit the activity of the radium emanation to die out after changing the air in the electroscope.

IV. Measurements in Airplanes and Balloons

Preliminary measurements made in captive balloons at Ross Field, near Pasadena, by one of us (Otis) yielded results in agreement with

those of other observers in that up to an altitude of 2000 meters the number of ions per cc per sec. was from 1 to 3 less than on the ground. No systematic change, however, was observed in this work at low altitudes.

The mean results of a long series of airplane flights made by Otis in 1922 at Marsh Field (near Riverside) and in 1923 at Rockwell Field (near San Diego) are shown in Table 1. These flights reached heights of more than 5000 meters. The numbers given are taken from a smooth curve drawn so as to fit as well as possible 17 observed points. In three

TABLE I

Airplane observations

Altitude	*Excess over ground*
500 meters	−2.1 ions/cc. sec.
760	−2.7
1200	−2.7
1750	−1.9
2500	−0.1
3400	+2.4
4200	+4.6
5200	+7.4

instances these points depart from the curve by as much as 2.5 ions, out of a total discharge-rate, at the high altitudes where these points lie, of from 17 to 19 ions. The accuracy is limited by the shortness of the time, usually a half hour, during which a given altitude was maintained.

In these airplane flights the electroscope was suspended in front of the observer's seat by three pieces of ordinary laboratory rubber tubing, attached at their upper ends to the sides of the cockpit or to the gun-mount. The instrument was kept from swinging by another piece of tubing fastened at one end to a plug which screwed into the bottom of the electroscope and at the other end to the floor of the cockpit. The electroscope was thus made stable and free from the effect of vibration of the airplane motor.

The method followed was to go to the highest altitude attainable in a reasonable time, maintain the airplane accurately at that altitude during the period over which ionization was to be measured, then drop down to the next altitude, etc. Because of the limit to the amount of gasoline that can be carried to those high altitudes and the long time required to reach them, it was never possible to make observations at more than three different altitudes on the same day.

The results shown in Table I are in agreement with those of Millikan and Bowen[1] in that they show a markedly lower rate of leak at the highest altitudes reached than those reported by Hess and Kolhörster. However, as a whole these balloon and airplane measurements are in agreement with those of the European observers *in showing that the*

intensity of the penetrating radiation first decreases to a minimum after which it increases continuously with altitude.

V. Independence of Penetrating Radiation upon Time of Day

During three different summers, 1922, 1923, 1925, we have made long series of observations, not only at Pasadena but on Mt. Whitney and on Pikes Peak, to test the constancy of the ionization due to the penetrating rays. At Pasadena, where the average number of ions as measured by the foregoing unshielded electroscope is 11.6, the fluctuations may be as much as an ion, but no systematic variation whatever has been observed. On Pikes Peak, where the rate of discharge of the unshielded electroscope is nearly twice that at Pasadena no variation with time of day was found.

Table II gives in the first two columns a series of readings, each lasting two hours, taken on top of Pikes Peak inside a shield of lead 4.8 cm thick at the sides, 11 cm at the top, and open at the bottom, and in the last two columns a continuous series of twenty similar observations taken with the unshielded electroscope at altitude 4130 m on the trail to Mt. Whitney.

Table II

Observations showing independence of penetrating radiation upon time of day.

	Pikes Peak (4300 m) Shielded electroscope				Mt. Whitney Trail (4130 m) Open electroscope			
	Mean time of observation		Ions per cm^3 per sec.		Mean time of observation		Ions per cm^3 per sec.	
9/22/23	2:43	P.M.	12.5	9/16/22	8:50	P.M.	19.2	
	4:57	"	12.4		10:58	"	18.9	
	7:06	"	12.1					
	9:26	"	12.7	9/17/22	1:05	A.M.	19.2	
9/23/23	11:31	A.M.	12.6		3:12	"	18.9	
	1:38	P.M.	12.2		5:19	"	19.2	
	4:05	"	12.8		7:26	"	20.0	
	8:35	"	12.0		9:31	"	20.7	
	10:45	"	12.0		11:37	"	19.4	
					1:43	P.M.	18.6	
9/24/23	12:57	A.M.	12.0		3:50	"	19.8	
	3:25	"	12.2		5:59	"	19.2	
	5:52	"	12.3		8:03	"	19.6	
					10:07	"	19.3	
		Mean,	12.3	9/18/22	12:12	A.M.	19.4	
					2:18	"	19.8	
					4:26	"	20.0	
					6:33	"	20.4	
					8:40	"	19.9	
					10:49	"	20.0	
					12:54	P.M.	21.0	
						Mean,	19.6	

The results shown in this table are merely typical of a very considerable amount of data, all of which is consistent in showing that within the limits

of our experimental error there is no dependence of the penetrating radiation upon daylight or darkness, or upon the position of any of the heavenly bodies. Two recent observations taken in a geological basin at a time when the Milky Way was wholly beneath the horizon gave no indication of a rate of discharge lower than that found when the Milky Way was overhead.

VI. Dependence of Penetrating Radiation upon Altitude

As already indicated, the mean value of the penetrating radiations as taken by the unshielded electroscope on the Institute campus is 11.6 ions. At bench mark No. 15 of the U. S. Geological Survey on the Mt. Whitney Trail, altitude 4130 m it is 19.6. At bench mark No. 14, elevation 3660 m, the mean of two observations gave 17.3 ions. The last two observations were both taken on the granite rocks so that their difference, 2.3 ions, might be expected to represent a true altitude difference. *It is quite close to the difference shown in Table I in the readings taken in airplanes between the same levels.* Further, near bench mark No. 14 a shallow lake 1 m deep was found over which when the electroscope was floated on a raft the reading was 13.6, or 3.7 ions less than on the adjacent rocks. This difference is close to the mean of all the data heretofore collected on the change in electroscope reading in going from over land to over water. A collection of eight such differences taken by McLennan, McLeod, Kunsman, and Wulf is as follows: 3.3, 5.1, 3.8, 2.2, 4.9, 3.2, 3.8, 4.5; mean 3.8. This mean is in close agreement with the value of 3.7 here found. When 3.7 is subtracted from any of the aforementioned mountain observations they come fairly close to the readings at corresponding heights shown in Table I.

Although, then, the uncertainty due to variability in the activity of the adjacent rocks is great, *the evidence of all the foregoing mountain and airplane work is that there is a definite variation with altitude alone and that mountain and airplane observations can be brought into approximate agreement by suitable precautions for eliminating the activity of the adjacent rocks.*

VII. Absorption Experiments on Pikes Peak

None of our experiments so far had given us any information about the actual hardness of the penetrating rays. To obtain this information we constructed a completely encircling shield of seven sheets of lead, each a little less than 7 mm thick, the total lead shield having a thickness of 4.8 cm. The sides of the shield were made of semicylinders removable separately so as to open the electroscope to radiations from opposite directions. The top and bottom shields were circular plates of the same sheet lead.

In order to support this 300 pounds of lead it was necessary to use a steel frame consisting of two vertical rods supporting two ring-shaped plates. On the bottom plate rested the electroscope and the sides of the shield, while the top plate held the top of the shield. The bottom

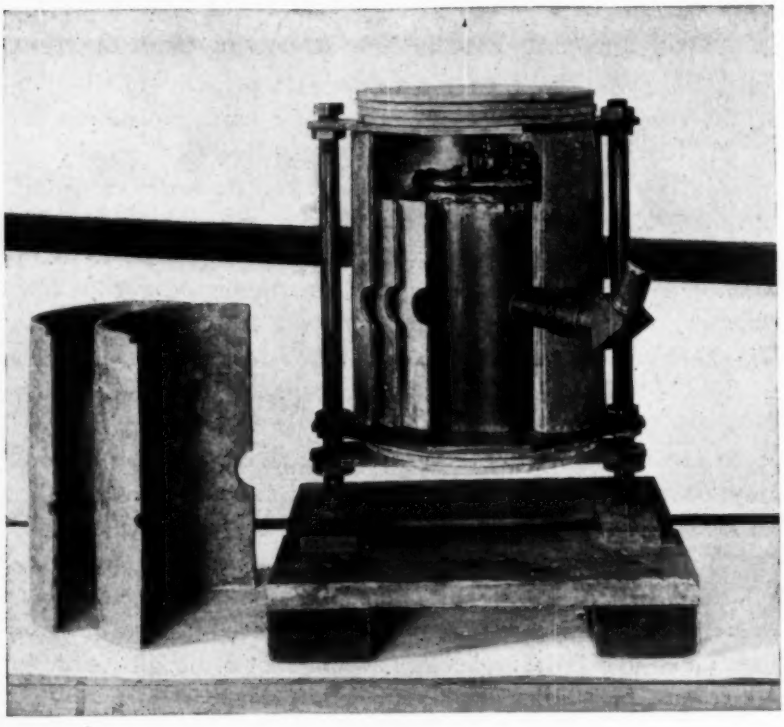


Fig. 3

of the shield was placed on a steel strip and brought up to the bottom of the electroscope by nuts on the vertical rods. In Fig. 3 the electroscope is shown on its stand with part of the lead sheathing in place.

TABLE III

Pike's Peak observations—out-of-doors.

A	Unshielded (mean of four one-hour runs)	23.2 ions per cm³ per sec.
B	Shielded (4.8 cm of Pb.) (mean of four one-hour runs)	11.6
C	Top only unshielded (mean of three one-hour runs)	12.3
D	Bottom only unshielded (mean of four one-hour runs)	13.2
E	North side only unshielded (mean of four one-hour runs)	16.9
F	South side only unshielded (mean of four one-hour runs)	16.7
G	Both sides unshielded (mean of two one-hour runs).	20.55
H	On the tower (17 m high) of the building, unshielded, mean of two observations (17.1 and 17.5)	17.3

The results of all the observations taken on Pikes Peak are condensed into Tables III and IV. In Table III measurements *A* to *G* were taken

out of doors on the rocks at the top of Pikes Peak. Measurement *H* was taken on the top of the skeleton steel tower above the inn. The measurements of Table IV were made inside the inn. The means of observations taken with the same apparatus in a tent on the campus of the Institute at Pasadena are given in Table V.

TABLE IV

Pikes Peak observations—indoors.

	Unshielded A	Shielded B	Top and bottom unshielded C	Bottom unshielded 16 layers on top D
		(Before the storm)		
	22.51	12.36	14.00	12.10
		12.23	15.04	12.60
		12.00	14.42	12.20
		12.63	14.54	12.80
Means	22.51	12.30	14.50	12.43
		(After the storm)		
	20.78	10.94	12.67	12.35
		11.11	12.70	11.75
			12.74	
			12.92	
			12.77	
Means	20.78	11.03	12.76	12.05

TABLE V

Pasadena observations

A	Unshielded	11.57
B	Shielded	9.37
C	Top only unshielded	9.54
D	Bottom only unshielded	9.40
E	Top and bottom unshielded	9.54
F	Both sides unshielded	10.75
G	Sides shielded, bottom unshielded, 16 layers of lead on top	9.28

There is no evidence in Table III of any difference in intensity of the penetrating radiations coming from the north and from the south, for the difference between the ionizations when the north side was unshielded and when the south side was unshielded is well within the limits of experimental error. The data show also that most of the radiation entered the electroscope through the sides, as was to be expected.

Another interesting result is that on Pikes Peak, the radiation out-of-doors was greater than that in-doors, while in Pasadena the radiation out-of-doors is a little over 1 ion per cc per sec. less than that in-doors in a concrete building. At Pasadena, then, the walls of the building add more radiation than they absorb from the outside, while on Pikes

Peak the reverse was true. This is doubtless because on Pikes Peak there is more outside radiation to absorb.

The radiation found on Pikes Peak is in substantial agreement with the measurements made at corresponding heights both on Mount Whitney and in airplanes. Thus, if the amount of radiation from the ground be taken the same as on Mount Whitney (3.7), then, following the same method as was used above, the radiation which would have been observed at the altitude of Pikes Peak (4300 m) if the ground had not contributed anything is, from the mean of all the A measurements in Tables III and IV, $22.2-3.7$ or 18.5 ions per cc per sec. The difference between this and that observed at Pasadena, from A, Table V, is $18.5-11.6$ or 6.9 ions per cc per sec. On referring to Table I it will be seen that this value fits reasonably well with the airplane data.

But it is obvious at once from Table III that there is a very much larger amount of soft radiation (of the hardness of gamma rays) on the mountain peaks than at Pasadena. Thus, while the difference between the shielded and the unshielded readings at Pasadena is but $11.57-9.37$ or 2.20 ions, on the Peak outdoors it is $23.2-11.57$ or 11.6[3], and when means are taken as above it is $22.2-11.57$ or 10.6[3]. The rays producing these 11.63 (or 10.63) new ions found (unshielded) on Pikes Peak are necessarily soft rays since they are nearly all absorbed by the lead screen within which there are found all told but 2.23 more ions than at Pasadena. If these new rays found on Pikes Peak are assumed to be homogeneous, their absorption coefficient, α, computed from the relation $I=I_0e^{-\alpha d}$, comes out, since d, in meters of water, is $4.8\times11.3\div100=0.54$,

$$\alpha=\log_e(11.63/2.23)\div0.54=3.1 \text{ per meter of water.}$$

This indicates that these rays are but little harder than the gamma rays from RaC, which are taken by Kolhörster,[2] for example, as having a coefficient of 3.9 per meter of water, while for ThD $\alpha=3.3$. *In other words, a homogeneous radiation of about the hardness of the gamma rays from* RaC *or* ThD *would account for all the increase found inside and outside of lead screens in the Pikes Peak experiments. If the rays are not homogeneous, since, in any case 80% are absorbed in the lead, the great majority of them cannot be appreciably harder than gamma rays, and these must be of local origin since gamma rays are all absorbed in 500 meters or so of air.* The change from about 22 ions to 17.3 ions in going from the inn to the fifty-foot tower above it indicates that some of the new rays found on the Peak are softer than gamma rays.

[2] Kolhörster, Sitz. Ber. d. Preuss. Akad. **34**, 371 (1923).

The foregoing evidence for the local origin of the greater part of the increased radiation found at the Peak is strengthened by a consideration of the effect of the storm noted in Table IV. This was a heavy snow storm, in which perhaps a foot of snow fell. The storm began at about six o'clock one evening and lasted throughout the night. About ten o'clock P.M. we noticed the reduction in the readings, a reduction which persisted during the hours during which we kept observing continuously after the storm. We had been observing day and night for two or three days before the storm, and had obtained a consistent series of readings throughout, so that the change surprised us greatly when it came. Table IV shows that all the readings, shielded and unshielded, are smaller after the storm than before. These readings were all taken indoors where the temperature was kept essentially constant, and no instrumental causes of the change could be found.

If these changes are due to the storm, i.e., to the blanketing of the earth with snow, they should be essentially the same in the column headed *B* as in that headed *D*. Taking, then, the mean of these two changes we obtain as the average shielded reading after the storm 11.5. The change under *C*, which is somewhat too large to be altogether consistent with the changes under *A*, *B*, and *D*, forces one to admit a somewhat larger observational or instrumental error of some sort than the general consistency of the readings otherwise indicates. Nevertheless, the readings as they stand, taking 11.5 as the mean shielded reading after the storm, show a drop due to the storm of about 8 percent for the unshielded condition and 7 percent for the shielded condition. When further we subtract from both readings the 6 or 7 ions which, according to our measurements made under water, were due to the radioactivity of the walls of the vessel and hence had nothing to do with external radiations at all, we see that the rays which get through the lead screen are cut down by the storm by quite as large a percent (apparently a slightly larger one) as the rays found in the unshielded electroscope. Such a result, if correct, *obviously requires the rays to be entirely of local origin.*

Both lines of evidence presented above point, then, to the conclusion that there is on mountain peaks a copious radiation of local origin and of a hardness not greater than that of the gamma rays of radium or thorium, but they reveal thus far no penetrating radiation of cosmic origin. If such a radiation exists at all it can at the most produce but a small part of the ionization observed in electroscopes on mountain peaks.

Kolhörster[3] in 1923 assumed such a radiation which produced 2 ions per cc per sec. at sea level, and had an absorption coefficient α in water of 0.25 per meter. Such a radiation would produce at Pikes Peak, where the average barometer reading is 17.5 inches, an ionization I_0 given by

$$\tfrac{1}{2}I_0 = e^{.25\times 4.3} = e^{1.08}$$

Therefore,

$$I_0 = 2\times 2.95 = 5.9$$

and of these 5.9 ions 5.15 would have been found inside our lead screen 4.8 cm thick. Similarly of the 2 ions assumed at sea level to be due to the cosmic rays 1.75 would be found inside the lead screen. That is, radiation of the assumed characteristics would have caused by itself inside our lead screen an increase of $5.15-1.75=3.4$ in taking the screened electroscope to the top of Pikes Peak even if none of the large increase in radiation shown by the unshielded observations on the Peak got through the lead—a supposition well nigh certain to be contrary to fact, for gamma rays from ThD would pass through this lead to the extent of about one sixth of the value outside.

The observed increase inside the lead screen and outdoors on the peak was, however, but 2.23 ions, that indoors after the storm but 2.13 and that indoors before the storm 2.9, a mean of 2.4 in place of the required minimum value of 3.4. In other words, penetrating cosmic rays of such characteristics as were assumed above cannot exist, since these rays alone, without the aid of any local radiation such as almost certainly exists, would produce on Pikes Peak a 40 percent greater increase in ionization inside the lead shield than we found. *The net result of the Pikes Peak work is, then, to establish quite definitely* (1) *the existence of a considerable increase in soft radiation in ascending from Pasadena to the Peak*; (2) *the non-existence of a radiation of cosmic origin of such constants as are supposed above.*

If cosmic rays exist at all they must be less intense at the surface than above assumed, or else they must be more penetrating than any one had as yet suggested.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
March 1, 1926.

[3] Kolhörster, Sitz. Ber. D. Preuss. Akad. **34**, 366 (1923).

VARIATION WITH PRESSURE OF THE RESIDUAL IONIZATION IN GASES

By Wm. W. Merrymon

Abstract

The residual ionization in aged, dry, and dust free air, H_2, He, A, O_2, N_2, CO_2, CH_4 and C_2H_4 has been measured at pressures from 0 to 180 cm Hg. In order to reduce radio active contamination, a glass globe with a sputtered silver coating was used as the ionization chamber. An electrometer and compensation devices eliminated the effect of fluctuations in the battery and provided a null method that kept the guard ring at the same potential as the collecting system, thus eliminating leakage. The ionization curves show a more rapid rise in the lower pressures which ceases at from 15 to 65 cm Hg, when the alpha-rays causing it are absorbed. Above this the curves are straight lines. From these portions the increase in ions formed per cc per sec. per atm. has been determined. It is least in the case of hydrogen (2.033), and largest in the case of argon (18.59). This rate divided by the number of electrons in the molecule is approximately constant (0.855). The rather good agreement with Kleeman's beta-ray results might be regarded as an indication that the principal agency operative was of a beta-ray character.

Introduction

THE discovery about twenty-five years ago of the spontaneous formation of about 8 or 9 ions per cc per second continuously in air inclosed in sealed containers, called the residual or natural ionization, led to much work of investigation as to its properties—the effects of the kind of metal in the ionization chamber,[1] of the temperature,[2] as well as the change observed upon shielding by metals, water, etc.[3] These experiments showed conclusively that the observed effect at the surface of the earth was a composite one in which rays from radioactive substances in the ground, atmosphere, the building, and above all, radioactive contamination in the chamber itself, played a large part. McLennan and Murray[4] reduced the number of ions formed to only 2.6 per cc per sec. by using an ionization chamber made of ice on Lake Ontario when frozen over. Certain observations by Hess and Kolhörster in Europe and confirmed by Millikan and Bowen in America,[5] show an increasing rate of ion formation at high altitudes.

[1] McLennan, Phil. Mag. **14**, 760 and 779 (1907); Phys. Rev. **26**, 526 (1908).
[2] Patterson, Phil. Mag. **6**, 231 (1903); Kingdon, Phil. Mag. **32**, 400 (1916).
[3] McLennan and Burton, Phil. Mag. **5**, 699 (1903);
Burton, Phys. Rev. **18**, 188 (1904);
Wright, Phil. Mag. **17**, 295 (1909).
[4] McLennan and Murray, Phil. Mag. **30**, 428 (1915).
[5] Wigand, Phys. Zeits. **18**, 445–463 (Sept. 15, 1924); Millikan and Bowen, Phys. Rev. **27**, 353 (1926).

This suggests a cosmical origin for a radiation of a penetrating power some seven times as great as any known radioactive rays. Swann[6] and others have considered theoretically the origin of a very penetrating radiation such as this supposed cosmical one, and he has also discussed the several results to be expected from such a primary ionizing source.

Most of the work done has been on air and at atmospheric pressure, although since the beginning of interest in the subject some observations have been made upon other gases,[7] principally hydrogen, carbon dioxide, and acetylene. Early observations showed that the rate of ion formation increased with the pressure, approximately proportional to it above atmospheric pressure. Recently Downey[8] and Fruth[9] have carried observations up to 75 atmospheres, and have found air, oxygen, and carbon dioxide to reach a constant value of ionization at about 50 atmospheres. Nitrogen, however, did not show this phenomenon although samples made by radically different methods were tried.

The purpose in the present work was to obtain a series of observations of the variation of the residual ionization with pressure in as many gases of an elementary kind as possible and under identical conditions. It was decided to try the use of an ionization chamber of glass with silver coating sputtered inside. By this means it was hoped to reduce the radio active contamination in the chamber, which is considerable in even the best metal vessels, and has been responsible for the distorted or discordant results of numerous observers. The nature of the chamber as constructed, particularly the stopper, limited the range of pressures from 0 to 180 cm of Hg.

Description of Apparatus

The general form and arrangement of the apparatus was suggested by Professor Swann, and is shown in Fig. 1. The parts *C* and *D* were used only in the auxiliary determination of the capacity-influence coefficient required for the computation. The switch K_c and the arrows from (5) in *C* to (1) indicate where the connection was made for these observations. During the taking of the regular data the small hole in the right-hand side of (3) was closed and the collecting system (1) was then entirely insulated and shielded. The ionization chamber *G* was a 5

[6] Swann, Phil. Mag. **47**, 306 (1924); Bull. Nat. Research Coun. No. 17, p. 66 (Mar., 1922).

[7] Jaffe, Phil. Mag. **8**, 556 (1904); Ann. der Physik (2) **28**, 326 (1909);
Wilson, Phil. Mag. **17**, 216 and 321 (1909);
McLennan and Trealeaven, Phil. Mag. **30**, 415 (1915).

[8] Downey, Phys. Rev. **16**, 420 (1920); **20**, 186 (1922).

[9] Fruth, Phys. Rev. **22**, 109 (1923); Broxon, Phys. Rev. **27**, 542 (1926).

liter, Pyrex, balloon flask with the neck cut off and ground down to the proportions shown. An auxiliary apparatus was used for sputtering the inside of the globe. The coating was quite uniform and of about 1/3 opacity over the globe, increasing to an opaque coat in the neck where electrical contact with the stopper had to be established. The central electrode or collecting rod in the globe was of glass and had also been sputtered with silver. It was attached by a brass rod inside it and a collar, to the stemrod which passed out through the stopper. Contact between the silver coatings of globe and rod, with the brass stopper and stem, respectively, were made with pieces of tinfoil. The arrangement of the guard ring in the stopper and of the gas inlet tube (p) were as shown.

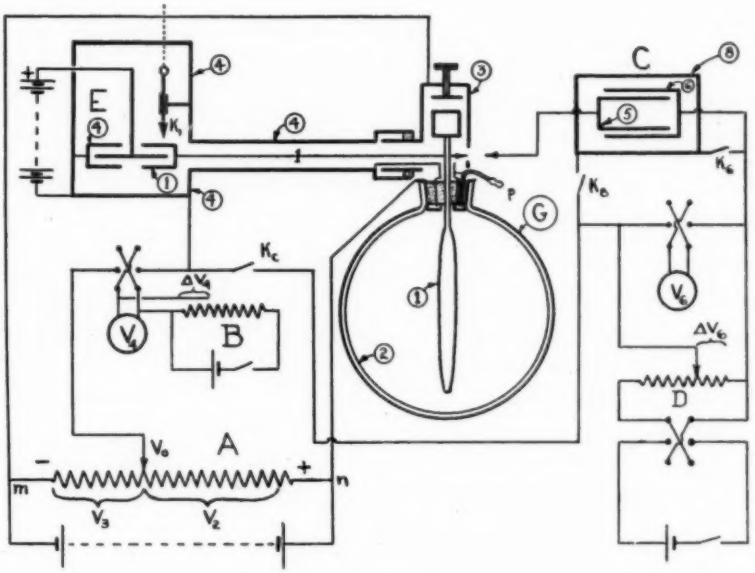


Fig. 1. Diagram of apparatus.

The upper end of the stem of the collecting rod was enlarged into a cylinder that fitted the cap (3) closely. This provided the auxiliary capacity for the compensation scheme suggested by Swann[10] for such observations. The disk in the top of (3) could be screwed down to adjust this capacity, and the point V_0 on the high resistance in A was varied until $V_3C_3 = V_2C_2$. The various capacities then compensate in their action and there is no inductive deflection of the needle due to fluctuations of the battery in A. The balance was subsequently maintained throughout the work by moving V_0 slightly, as required, so

[10] Swann, Phys. Rev. **17**, 240 (1921).

that the electrometer needle would defiect only a few millimeters upon throwing on or off the battery in A. The cap (3) was held by a hard-rubber collar (not shown) that fitted on the outside of the guard ring.

The high resistance in A was made by winding IAIA No. 40 wire on paper-wrapped sections of brass tubing $\frac{3}{8}$ by 9 inches long (1×23 cm). The total resistance of the 104 tubes used was 101,000 ohms. The resistance B was a cranking resistance of about 28 ohms used with a dry cell. The battery on the needle was a 100-volt silver-chloride set, as described by Erikson.[11] The battery in A was a 220-volt set of dry cells. Throughout the observations the point V_0 was such that V_2 was 178 volts, and V_3 was about 42 volts.

The electrometer was an ordinary Dolezalek instrument at a sensitivity of 1,000 mm per volt on a scale 130 cm distant. The whole of the apparatus was mounted on a large brick pier and, except for the part A, it was completely insulated from the pier by various plugs of sulfur to eliminate leakage between the parts. The insulating material in the stopper of the globe was of hard-rubber.

Method of Making Measurements

Usually the positive terminal of A was attached to the globe, and the collection of charge by the central system would raise its potential with respect to the other quadrant and case. By cranking B the potential of the case was raised ΔV_4 volts and so kept up to that of the collecting system, thus providing a null method. It is to be noted that by this method the potential of the collecting system and guard ring in the stopper were always the same, and hence leakage between them was practically eliminated.

Having brought the system to balance by suitable adjustment of the point of contact V_0, the taking of observations consisted in raising key K_1, bringing the spot of light to the zero point by cranking B, taking the starting time and initial reading V_4. As the charge collected the spot was held on the zero position by cranking B, and every few minutes a reading of the time and voltage on V_4 was made. The readings were continued in this way usually from 20 minutes to an hour, depending on the gas and pressure. During this interval a number of readings of time and V_4 would be made and the separate rates of leakage calculated. The accuracy attained was such that the series of results usually agreed among themselves to within a few hundredths of an ion per cc per sec.

Throughout the making of an observation,

$$V_1 = V_4 = V_0 + \Delta V_4.$$

[11] Erikson, J.O.S.A. and R.S.I. **8**, 549 (Apr., 1924).

At the start

$$Q_1 = c_{11}V_0 + c_{21}(V_0 + V_2) + c_{31}(V_0 + V_3) + c_{41}V_0.$$

At the close

$$Q_1 + \Delta Q_1 = c_{11}(V_0 + \Delta V_4) + c_{21}(V_0 + V_2) + c_{31}(V_0 + V_3) + c_{41}(V_0 + \Delta V_4).$$

Hence,

$$\Delta Q_1 = (c_{11} + c_{41})\Delta V_4.$$

Let q represent the number of pairs of ions formed per cc per second, Since

$$dQ/dt = \text{const.}\, dV/dt = (c_{11} + c_{41})\Delta V_4/t,$$

then

$$q \times G \times 4.774(10)^{-10} = (c_{11} + c_{41})(\Delta V_4/t) \times (1/300).$$

where G is the volume of the globe (5350 cc) and t the time in seconds since the start. As indicated below, the capacity-influence coefficient

$$(c_{11} + c_{41}) = 27.97 \text{ e.s.u.}$$

Therefore,

$$q = 3.65(10^4) \times \text{volts cranked in per second.}$$

The gases were introduced very slowly into the globe, usually up to the limit of pressure, and observations were made. Then the pressure was reduced a few centimeters and another observation was made; and so on for the series.

Subsidiary Measurements

It is very necessary in these observations to make sure that saturation voltages are used, and therefore preliminary observations were carried out which showed that a battery of 220 volts, which was used throughout the work, gave complete saturation. Trials were made with both the positive and negative end of the battery in A connected to the globe, and it was found that there was a constant slight difference between the two sets of results, the direction dependent upon the sign of the potential on the needle. This was due to the quadrant of the electrometer acting as an ionization chamber so that when the needle was positive and the positive terminal of A was on the coating of the globe, the resulting ionization observed was about 0.7 ion larger than when the negative terminal was attached to the coating. This was true throughout the range of pressures. The needle was kept positive throughout the observations here reported, and the coating was positive.

The cap (3) also acts as an ionization chamber and drives to the collecting system ions of sign opposite to those being collected in the globe. This together with that from the electrometer quadrants is practically constant throughout any one set of readings, depending, of course, upon the atmospheric conditions. Of these two, the effect due

to the cap is the larger and the two together constituted an extraneous current which opposed the charge being collected in the ionization chamber. At low pressures this becomes predominant. It is equal to the value of the ionization observed at zero pressure.

To test for this extraneous current, an observation would occasionally be made with the wire from n to the globe disconnected, and a wire from the negative terminal m joined to the coating. The extraneous current is one-half the sum of the current obtained by this connection and that as normally observed. Repeated observations throughout the range of pressures gave a constant result which agreed very closely with the current observed at zero pressure. Therefore, for determining the absolute values one seems warranted in supposing the curves raised until they terminate at zero ions with zero pressure. They have, however, been plotted just as observed, according to deflections to right or to left. The pressures are in centimeters of Hg and the ordinates show the number of pairs of ions formed per cc per second.

For the determination of the capacity-influence coefficient $(c_{11}+c_{41})$ the parts C and D of the apparatus were used. The condenser C was a Gerdien variable standard made by Gunther and Taegetmeyer and provided with calibration curves for both induction and capacity coefficients. When the shield (8) was connected to the electrometer case for observations, the influence coefficient c_{65} was involved. This was read from the calibration curve of the instrument for the particular setting used. With the shield connected to the outer coating (6) the capacity coefficient c_{55} was employed, and this was likewise scaled off from the other calibration curve. Both methods of connection were used for several settings of the instrument. The results agreed very closely throughout the range of pressures. The observation was made by raising K_1, then quickly introducing a fraction of a volt ΔV_6 and compensating the resulting deflection of the electrometer by cranking B. This method eliminated the effect of contact potential and hence the results were not influenced by the direction of the battery in D. The ratio of ΔV_6 to $\Delta V_4 \times c_{65}$(or c_{55} for the second method) gave $(c_{11}+c_{41})$. The average value was 27.97 e. s. u.

Results

The results of the observations are shown in Figs. 2, 3, 4, and 5. The gases used were from pressure tanks which had stood for at least one month so that the emanation content should have decayed to a negligible value. The gases were introduced into the evacuated globe through a long P_2O_5 drying tube and a similar tube filled with absor-

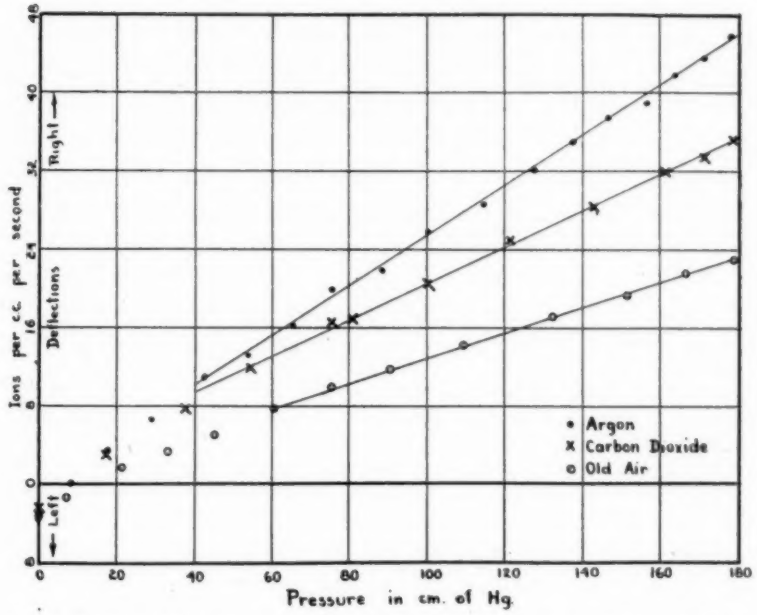


Fig. 2. Variation with pressure of the residual ionization in argon, carbon dioxide and old air.

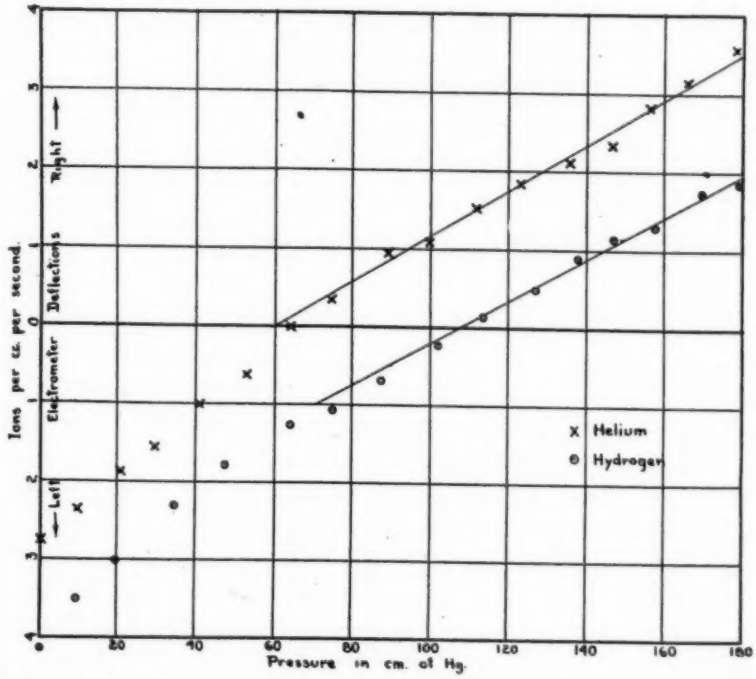


Fig. 3. Variation with pressure of the residual ionization in helium and hydrogen.

bent cotton to remove dust. With these precautions subsequent observations were found to agree to within the error of observation, about 0.2 ion per cc per second. In some cases the gases were left in the apparatus for weeks to see if they would show any decrease in activity, but none was found. Neither was there any increase in activity following their introduction. The observations could be stopped at any point and subsequently taken up and carried on again. The curves could be repeated, and many of them were taken two or three times.

The argon of Fig. 2 was held in the tank several months before use. The carbon dioxide was from the usual pressure tanks, and was known

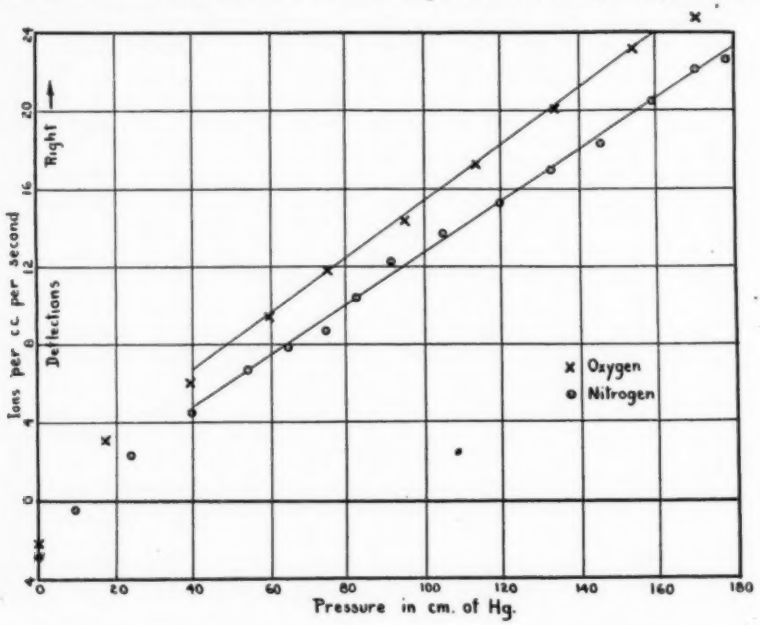


Fig. 4. Variation with pressure of the residual ionization in oxygen and nitrogen.

to be at least six months old. The old air was from a pressure tank that had been filled with dry, dust-free air five months previous to its use. The helium and hydrogen of Fig. 3 were from tanks that had been on hand for many months; the same is true for the oxygen and nitrogen of Fig. 4. As a check experiment, the helium and hydrogen were run through charcoal and spiral tubes immersed in liquid air, but no change in the results as compared with the former ones was found. The ethylene shown in Fig. 5 was known to be several months old, and the methane was at least six weeks old. The air from liquid air was obtained by placing some fresh liquid air in a Pyrex stoppered tube with side neck to lead off the evaporating air. The lower part of the tube was put

down into a flask of liquid air. As some of the air evaporated, it was led into the globe through the drying tubes. The results fulfilled the hope that air could be gotten at once that would behave like well aged air, as far as emanation is concerned, for any present should remain behind in the liquid state.

The numerical values of the results are given in Table 1. As above, q represents the number of pairs of ions formed per cc per second, and in column 2 the increase in q per atmosphere increase in pressure is given. In column 3 the value of q at atmospheric pressure is tabulated, and to facilitate comparisons this is given in column 4 on the basis of that for

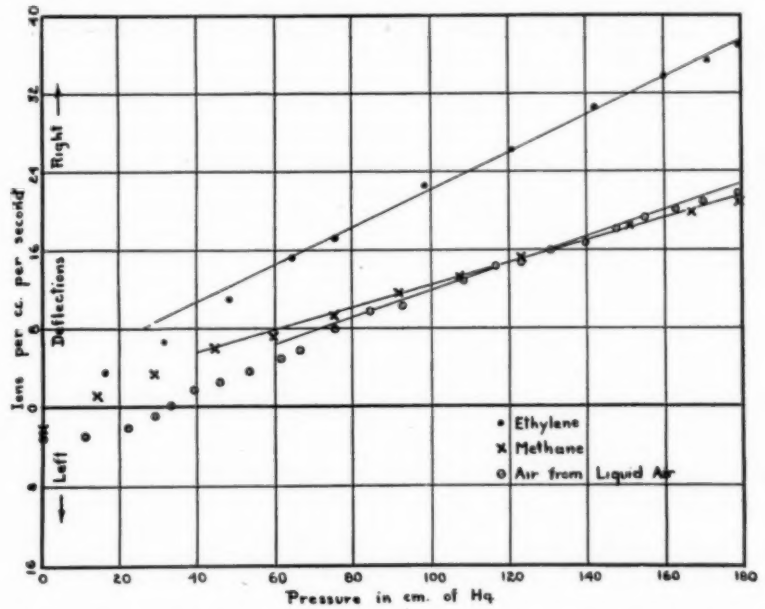


Fig. 5. Variation with pressure of the residual ionization in ethylene, methan and air from liquid air.

air = 100. Columns 4 to 8 incl. are for relative ionization at atmospheric pressure. Column 5 contains data from an early paper by C. T. R. Wilson[12] for the residual ionization in different gases. The data of column 6 for the natural ionization observed in the laboratory, and of column 7 for the ionization produced by alpha-rays are from a paper by McLennan and Trealeaven.[7] Column 8 contains data from a paper by Kleeman[13] for the relative ionization produced by beta-rays in different gases, and in this the values for nitrogen, methane, and ethylene were

[12] Wilson, Proc. Roy. Soc. **69**, 280 (1901).
[13] Kleeman, Proc. Roy. Soc. A. **79**, 231 (1907).

computed from the atomic ionizations as given in his table. This is in substantial agreement with similar data in a paper by R. J. Strutt[14] as well as in the above paper by McLennan and Trealeaven, although the data given for alpha-rays by the former authors differ rather pronouncedly from that of McLennan and Trealeaven, which was written a number of years later and has therefore been selected.

TABLE I

			Relative ionizations, air = (100)					
Gas	dq/atm	q at 76 cm	q for air = 100	Wilson	Mc L. and Treal.	Alpha-rays	Beta-rays, Kleeman	dq/atm electrons
H_2	2.033	5.0	41.0	18.4	22.6	56.0	16.5	1.016
He	2.215	3.2	26.2	.....	.....	.....	.....	1.108
CH_4	8.68	12.5	102.5	.....	.....	.....	118.0	.868
N_2	10.00	12.0	98.3	.....	.....	.....	95.0	.714
C_2H_4	14.70	20.2	165.5	.....	139.7	113.3	164.0	.919
Air	9.88	12.2	100.0	100.0	100.0	100.0	100.0	.707
O_2	10.95	14.2	116.4	.....	.....	.....	117.0	.685
A	18.59	22.8	187.0	.....	.....	.....	.....	1.033
CO_2	14.22	19.6	160.6	169.0	114.3	80.4	160.0	.647
							Mean =	0.855

DISCUSSION OF RESULTS

Effects from radioactive contamination in the walls and floors of a laboratory building can scarcely be avoided altogether, but it was believed that any such effects in these observations would be constant within the range of pressures used, and subsequent observations indicated that they were, at least within the error of observation. The effect of a trace of radioactive contamination within the ionization chamber itself would most probably be largely due to alpha-rays, but possibly also to beta-rays. The alpha-rays would be absorbed at less than one atmosphere in a chamber of the size used. The effect would therefore be to produce a current increasing proportionately with the pressure above vacuum until the rays completed their paths in the inclosed gas, and thereafter, a constant additive factor. The increased curvature in the lower parts of the curves is attributed to this cause, as has been done by G. Jaffe[7] in the case of his curves, and also by Downey.[8] The slope of the curves has been determined from their upper straight portions.

From a consideration of the curves it appears that in the case of each of the gases under residual ionization the increase per atmosphere of ion formation is characteristic of the gas in question, and is constant up to

[14] Strutt, Proc. Roy. Soc. A. **72**, 209 (1903);
Marx, Handbuch der Radiologie, Vol. I, p. 37; Vol. II, p. 40.

the limit of pressures employed. The attempts of some investigators[12] to relate this phenomenon to the density of the gases were not successful. That there is a close connection between the ionization in different gases and their electronic configuration has suggested itself. Found and Dushman[15] from their studies with the ionization gauge have felt that their observations indicated a quantitative relation between the ionization in different gases under electronic bombardment and the number of electrons in the molecule, or "molar number." There is entered in column 9 the increase in the residual ionization per atmosphere divided by the number of electrons in the molecule, assuming 14 for air. The results, although by no means of close uniformity, are at least suggestive. Hydrogen, the noble gases, and the heaviest one, carbon dioxide, depart the farthest from the mean, the former being 20 to 30 percent high and the latter 24 percent low.

Found and Dushman observed their results with hydrogen and helium to be higher than would be expected on such a basis, but their results for argon and carbon dioxide are not abnormal. Kossel[16] also found that the secondary ray production in hydrogen by electrons of 1000 volts was abnormally large, and that hydrogen retained this peculiarity when in combination. The data in column 9 likewise show methane and ethylene to be above the mean, but the differences suggest that the chemical bonding may also be a factor. Although the energy necessary to knock an electron from various atoms and from different parts of the same atom varies greatly, yet as a modifying condition may be mentioned Bohr's conception, "of the penetration, in the case of the less simple atoms, of electrons of highly elliptical orbits into the region inside the shells of lower quantum number, giving these penetrating electron orbits in some cases a smaller mean potential energy and therefore a higher stability, than some of the orbits corresponding to smaller quantum numbers."

If the ionization produced by the earth's penetrating radiation is to be compared to electronic ionization, it seems probable that it should be with that of high speed electrons. It may be of interest, nevertheless, to note that Hughes and Klein,[17] Jesse,[18] and Compton and Van Voorhis[19] using electrons of low velocity for producing ionization, do not

[15] Dushman, "High Vacua," p. 121;
Found and Dushman, Phys. Rev. **23**, 734 (1924).
[16] Kossel, Ann. d. Physik **37**, 393 (1912).
[17] Hughes and Klein, Phys. Rev. **23**, 450 (1924).
[18] Jesse, Phys. Rev. **26**, 208 (1925).
[19] Compton and Van Voorhis, Phys. Rev. **26**, 452 (1925).

find their results to support Dushman's suggestion as a quantitative relation. In Jesse's results He, A, CO, and N_2 would be practically together on the basis of the number of electrons in their molecules, but Ne was about 60 percent below and CH_4 and H_2 about 45 percent and 90 percent respectively above the mean of the first four. However, as suggested by Compton and Van Voorhis, it may be that the Dushman relation is more accurate at higher voltages—as might be expected on theoretical grounds and as is indicated by the work of Kossel, who made the same suggestion on the basis of his measurements at 1000 volts. McCallum and Focken[20] found that the increased ionization with higher voltages is much larger in neon than in the diatomic gases, hydrogen and nitrogen. The effect of higher accelerating potentials in increasing the ionization in neon relative to the others is also evident in Jesse's data.

Downey[8] and Fruth[9] found that the variation in the natural ionization of gases with pressure obeys a linear law up to more than 20 atmospheres, and they give the increase in ionization for air as from 1.23 to 1.58 ions per cc per sec. per atmosphere increase in pressure. The increase per atmosphere for air as observed here is much larger than they report. This might be explained as due to a beta-radiation within the chamber, or gamma-rays from the walls of the room. However, it is about the same proportion of the value at one atmosphere as was observed by McLennan and Burton.[3] Judging by Fruth's curves for O_2 and prepared N_2, his increase for O_2 is about 1/10 greater than that for N_2, which proportion agrees with the data in column 3 of the table. The value of q obtained for air at atmospheric pressure is about the same as Downey and Fruth observed, and lies between those for O_2 and N_2. McLennan and Murray[4] observed 7.6 ions with the best zinc chamber in buildings entirely free from contamination. The same chamber gave only 4.65 ions per cc per sec. on the ice over Lake Ontario. This indicates the degree of influence to be expected even in selected buildings.

The experimental curves agree in general with those of C. T. R. Wilson[12] for the spontaneous ionization in several gases. His vessel was smaller, and his curves do not all extend even to atmospheric pressure. He also noted the decrease in slope of his curves at pressures approaching one atmosphere, but regarded the significant part of his curves as that below this point.

The fact that the data of column 6 is uniformally lower than that of column 4 would suggest that the location in which McLennan and

[20] McCallum and Focken, Phil. Mag. 49, 1318 (1925).

Trealeaven made their observations had greater freedom from radioactive contamination. It is also true that in the case of both H_2 and He the presence of small amounts of other gases affect the ionization to a relatively greater extent. This might account for the apparently high value for H_2 in column 4.

The ionization for beta-rays and gamma-rays is about the same for the lighter gases, but for the heavier gases the gamma-ray ionization becomes much larger than that for beta-rays, because of secondary radiation of the beta and gamma type from the walls of the vessel and from the gas. Ionization with alpha-rays, as indicated in column 7 is quite different from the others; the ionization in H_2 is much greater, and in CO_2, C_2H_4 and N_2O considerably less, than that for the natural ionization or for beta-ray ionization. The somewhat better agreement between columns 4 and 8 might be taken as an indication that the residual ionization as observed is due chiefly to the effects of a radiation of a beta-ray character. It might be objected that comparisons with beta-rays should be made not of q but rather dq, since q involves alpha-rays. However, the beta-ray data quoted did not give values of dq, and furthermore, it seems probable that they also involved alpha-ray contamination to at least as great an extent as in the case of these observations.

The use of a glass vessel with sputtered coating (aside from the limitation it may place upon pressure) appears to be an advantage, and it would be of interest to employ vessels of different coatings particularly ones more resistent to active gases. It would be desirable for the vessel to be larger than this one and capable of standing several atmospheres pressure.

In conclusion the writer wishes to acknowledge his indebtedness to the members of the Ryerson Faculty, particularly to Professor W. F. G. Swann who initiated the work and method, and to Professor A. J. Dempster for his suggestions and the direction of the research during the last year. The observations here reported were made prior to June, 1925.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
December 30, 1925.

NOTE ON THE DECAY OF RaE*

By L. F. Curtiss†

Abstract

The decay of the activity of a preparation of RaE shown to be quite free from RaD has been observed over a period of 45 days. The *half period*, determined by the method of least squares, for this sample was 5.07 days. This value agrees with measurements by Antonoff, Meitner, and Bastings, but it is in disagreement with the value of 4.85 days determined by Thaller and recently observed by Fournier. It appears that the value given by Thaller, and previously accepted, cannot be correct.

SINCE 1912 the value 4.85 days has been accepted for the half period of RaE, based on measurements by Thaller.[1] Recently Bastings[2] redetermined the half period and found a value considerably higher. The mean of measurements on several sources gave 4.98 days. The latter determination however has been questioned by Fournier,[3] who observed the activity of three different sources and concluded that the value given by Thaller is correct. Obviously it is desirable to know the rate of decay of RaE with greater certainty than this disagreement permits.

In order to investigate this question, I have prepared a source of RaE and have observed its activity over a period of several weeks. Of course it is important to obtain a source as free as possible from RaD, the parent product. The RaE was obtained electrolytically on a platinum electrode from a RaE solution prepared from old radon tubes.± Conditions were adjusted so that the RaE should go to the cathode. The deposit was tested for RaD by exposing in a beta-ray spectrograph with the field properly adjusted to throw the RaD spectrum on the plate. A twelve hour exposure gave a very faint trace of the strong RaD line whereas an exposure of about three hours with the anode from the above electrolysis gave the complete spectrum. The deposit was then dissolved from the cathode by dilute HCl and the RaE obtained by rotating a nickel disk for about thirty minutes in this solution. Since little RaD was present in this solution we might expect the nickel disk to be fairly free from it. Measurements of the residual activity of the source after fifty days proved this to be the case, as is indicated in

* Published by permission of the Director of the Bureau of Standards, Department of Commerce.

† National Research Fellow.

[1] R. Thaller, Wien Ber., **121**, 1611 (1912).

[2] L. Bastings, Phil. Mag. **48**, 1075 (1924).

[3] G. Fournier, Comptes Rendus **181**, 502 (1925).

± I wish to thank Dr. Lind of the Fixed Nitrogen Laboratory for supplying this material.

the table. The nickel disk was mounted 15 cm below the face of a beta-ray electroscope as shown in Fig. 1 at *S*. It was left in position throughout the observations. A shutter *B* of lead 3 mm thick could be introduced in order to determine the natural leak from time to time. The foil *F*, in the lower face of the electroscope, was of aluminum 0.060 mm in thickness. Careful observations of temperature and of barometric pressure made it possible to reduce all readings to standard condi-

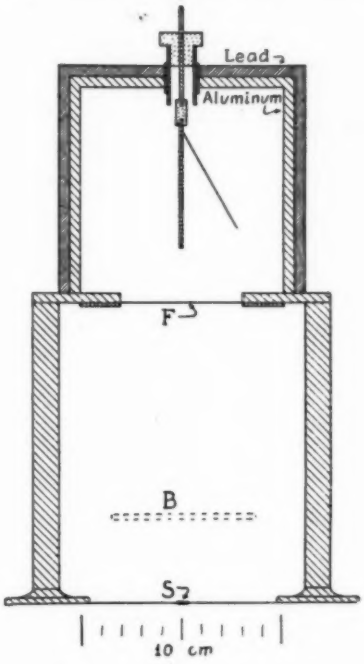


Fig. 1. Beta-ray electroscope.

tions. Table 1 gives the readings obtained, corrected for natural leak, temperature and pressure. It will be seen that at the end of 45 days the activity had become practically zero, indicating that very little RaD is present.

TABLE I

Decay of activity of RaE

Hours	*I*	Log$_e$ *I*	Hours	*I*	Log$_e$ *I*	Hours	*I*	Log$_e$ *I*
0.0	42.5	3.749	126.3	20.1	3.000	264.0	9.4	2.241
20.0	37.1	3.617	139.8	19.0	2.939	288.9	8.1	2.092
22.4	36.8	3.605	165.5	16.5	2.803	314.5	6.5	1.872
42.8	33.2	3.502	187.0	14.8	2.694	345.25	6.0	1.792
70.0	28.6	3.353	213.6	12.4	2.517	1080.	0.06	.....
91.8	24.7	3.206	244.0	10.4	2.341	.....	....	.....

The results are shown graphically in Fig. 2 where the logarithm of the observed activity has been plotted against the time. The slope has

been determined by the method of least squares. This calculation gives a half period of 5.07 days. The values obtained by Bastings for different sources were as follows: 5.04, 4.96, 5.02, 5.02, 4.98, 4.97, 4.96. It is evident that my observation agrees fairly well with his measurements and cannot be reconciled with Thaller's determination, or with that by Fournier. It may be well to recall that for various preparations Thaller obtained half periods ranging from 4.6 to 5.0 days and that presumably the accuracy of his measurements was not very high. The value 5.0 days has also been observed by Antonoff[4] as well as by Meitner.[5] The

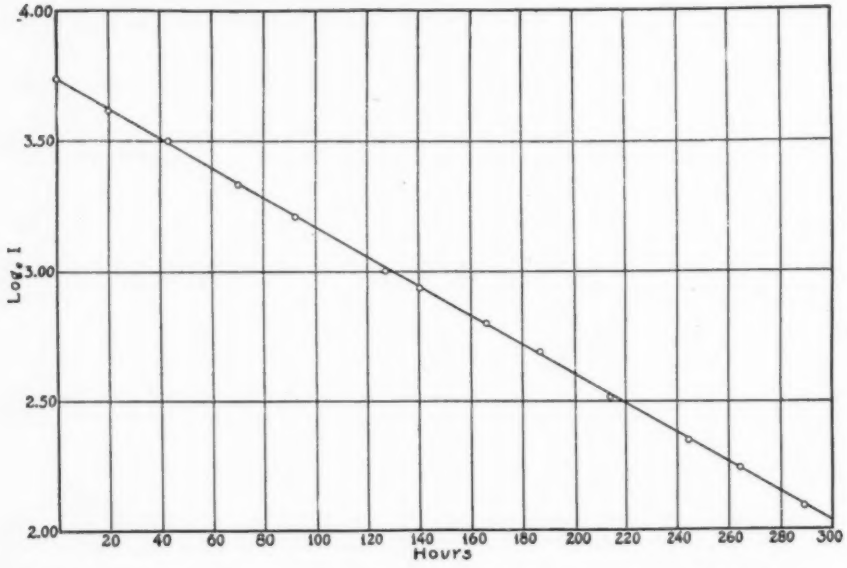


Fig. 2. Curve showing variation of the logarithm of the activity with the time.

evidence thus far seems to favor a half period much nearer five days than that heretofore accepted. The value given by Bastings may rather be too low than, as Fournier states, too high.

Of course the writer is aware that the value reported here may well be too high. However it is difficult to see how, in view of the precautions taken and the consistency of the observations, it can be in error by more than 1 percent. Even granting that the error may be as great as this, there is still no possibility of agreement with Thaller's value. Further work is in progress.

BUREAU OF STANDARDS,
WASHINGTON, D. C.
February 15, 1926.

[4] Antonoff, Phil. Mag. **19**, 825 (1910).
[5] L. Meitner, Phys. Zeits. **12**, 1094 (1911).

THE RATIO OF THE MODIFIED TO THE TOTAL SCATTERING COEFFICIENT OF X-RAYS

By O. K. De Foe

Abstract

Use has been made of the fact that the modified portion of scattered x-rays has not only a greater wave-length but also a greater absorption coefficient than the primary x-rays in order to separate the modified and unmodified portions of a scattered x-ray beam. The method involves the change in the intensity of scattered x-rays when a given thickness of aluminum is transferred from the primary to the scattered beam. Using a balance method, measurements of the ratio of the modified to the total scattering coefficient have been made for x-rays of wave-lengths 0.27A to 0.58A scattered from carbon, aluminum and copper at angles varying from 60° to 130°. *Comparison with theory.* Jauncey's theory predicts that the ratio should become unity when vers $\phi = 242\lambda_0^2/\lambda_\phi$ (λ_ϕ and λ_0 being measured in Angstroms). For carbon at 60° and 90° the experimental ratio becomes unity at wave-lengths of 0.32A and 0.46A respectively: The theory gives 0.31A and 0.44A respectively. A calculation of the modified scattering coefficient for copper at 90° for $\lambda = 0.4$A gives $0.71s_0$ (where s_0 is the Thomson coefficient at 90°), while the theory gives $0.74s_0$. Thus as far as they go the experiments are in agreement with the theory.

1. Introduction

A. H. COMPTON[1] has shown theoretically that x-rays scattered at an angle should be changed in wave-length by an amount given by the formula

$$\lambda_\phi - \lambda_0 = h/mc \text{ vers } \phi = .024 \text{ vers } \phi \qquad (1)$$

This value is derived on the ssumption that the electrons which do the scattering are free and at rest. Experiments by Compton,[2] Ross,[3] and others confirm this result but show also unmodified scattering which the theory does not predict. The existence of the unmodified line necessitates the definition of two scattering coefficients, one for the modified and the other for the unmodified portion. Previous determinations of the scattering coefficients give approximately the sum of these two coefficients. Throughout this article we shall denote by σ_1 and σ_2 the spherical linear scattering coefficient for the unmodified and modified x-rays respectively; while s_1 and s_2 will be used to denote the linear scattering coefficient per unit solid angle in the direction ϕ with respect to the forward direction of the primary rays

[1] A. H. Compton, Phys. Rev. **21**, 483 (1923).
[2] A. H. Compton, Phys. Rev. **22**, 408 (1923).
[3] P. A. Ross, Proc. Nat. Acad. Sci. **9**, 246 (1923); **10**, 304 (1924).

for the unmodified and modified x-rays respectively. If the primary x-rays are unpolarized the quantities σ_1 and s_1 are connected by the relation

$$\sigma_1=\int_0^{\pi} 2\pi s_1 \sin\phi\, d\phi \tag{2}$$

while a similar relation exists between σ_2 and s_2.

Jauncey[4,5] has proposed a theory which explains not only the presence of the unmodified line but also the width of the modified line. This theory takes into account both the motion and the binding energy of a scattering electron in its orbit and it gives a formula for the fraction of the total number of electrons which are in orbital positions such as to scatter modified x-rays in a direction ϕ. If we denote this fraction by $p(\phi)$ and use a subscript to denote the orbit which is occupied by the electrons considered, (for example $p_K(\phi)$ denotes the fraction of K electrons which are in a position to scatter modified x-rays in the direction ϕ then $p_K(\phi)$ is approximately given by

$$p_K(\phi)=\frac{\alpha_0 \operatorname{vers}\phi+2\sqrt{2\alpha_s}\sin\tfrac{1}{2}\phi-\lambda_0/\lambda_s}{4\sqrt{2\alpha_s}\sin\tfrac{1}{2}\phi} \tag{3}$$

where $\alpha_s=h/mc\lambda_s$, $\alpha_0=h/mc\lambda_0$, λ_s denotes the K critical absorption wave-length of the scattering substance, λ_0 the wave-length of the incident radiation and ϕ the direction of scattering. The values of $p_L(\phi)$, $p_M(\phi)$, etc., are obtained by means of similar formulas, when the orbits are circular and by more complicated formulas in the case of elliptic orbits.[5,7] $p(\phi)$ is now obtained as a weighted mean of the values for the various orbits. Jauncey and DeFoe[6] have shown that the theoretical value of s_2 is given by

$$s_2=\frac{Kp(\phi)\{1+\cos^2\phi+2\alpha_0(1+\alpha_0)\operatorname{vers}\phi\}}{2(1+\alpha_0 \operatorname{vers}\phi)^5} \tag{4}$$

where K is given by

$$K=(NZ\rho/W)(e^4/m^2c^4)\ . \tag{5}$$

In Eq. (5) N denotes Avogadro's number, Z the number of electrons per molecule, ρ the density, W the molecular weight of the scattering substance, e the electronic charge, m the mass of an electron, and c

[4] G. E. M. Jauncey, Phys. Rev. **25**, 314 (1925).
[5] G. E. M. Jauncey, Phys. Rev. **25**, 723 (1925).
[6] Jauncey and De Foe, Phil. Mag. **1**, 711 (1926).
[7] G. E. M. Jauncey, Phys. Rev. **27**, 687 (1926).

the velocity of light in vacuo. Jauncey and DeFoe[6] have pointed out that although s_2 should be given by Eq. (4) yet it is not a necessary result of the theory that s_1 should be given by replacing the factor $p(\phi)$ in the right side of Eq. (4) by $\{1-p(\phi)\}$. This could only be done if the probability of an electron's scattering in the direction ϕ were the same irrespective of whether the electron was in a position to scatter modified or unmodified rays. If the ratio s_1/s_2 can be measured experimentally, then Jauncey[7] has shown that the ratio of the probability P_U that an electron will scatter in a direction ϕ when in a position to scatter unmodified rays to the probability P_M that it will scatter modified rays is given by

$$P_U/P_M=(s_1/s_2)\,(p(\phi)/\{1-p(\phi)\} \tag{6}$$

The experiments of Barkla and Ayers,[8] Hewlett,[9] and Jauncey and May[10] show that there is scattering considerably in excess of the Thomson[11] value at $\phi=30°$ in the case of scattering by light elements. On Jauncey's theory however it is at 30° that the fraction $\{1-p(\phi)\}$ becomes considerable and therefore a considerable portion of the scattered rays are unmodified. Further, Barkla and Dunlop[12] find considerable excess scattering from heavy elements such as copper even when $\phi=90°$. Here again the fraction $\{1-p(\phi)\}$ becomes large when $\phi=90°$ when x-rays are scattered by copper. Again Hewlett[9] and Jauncey and May[10] find that when x-rays are scattered by light elements the scattering goes to zero at about $\phi=5°$. At this angle $p(\phi)$ vanishes. It seems then that excess scattering and also the zero scattering at small angles is a property of the unmodified scattering and not of the modified scattering. It is therefore evident that it is important to measure s_1 and s_2 experimentally, so that we may test the theoretical formula, Eq. (4), and also so that we may obtain s_1 as an empirical function of ϕ. As a preliminary attack on this problem the experimental values of $s_2/(s_1+s_2)$ have been determined for different scattering substances, different wave-lengths and for different angles of scattering.

2. Theory of the Experimental Method

The experimental value of the scattering coefficient σ_{exp} determined by previous observers has always been approximately the sum of the

[8] Barkla and Ayres, Phil. Mag. **21**, 275 (1912).
[9] C. W. Hewlett, Phys. Rev. **20**, 688 (1922).
[10] Jauncey and May, Phys. Rev. **23**, 128 (1924).
[11] J. J. Thomson, Conduction of Electricity through Gases 2nd Ed., p. 325.
[12] Barkla and Dunlop, Phil. Mag. **31**, 222 (1916).

two scattering coefficients σ_1 and σ_2. In the determination of σ_{exp} there is a slight error introduced by assuming the same absorption coefficient for the scattered as for the primary radiation, whereas in fact there is a slight increase in the absorption coefficient as shown experimentally by Sadler and Mesham.[13] This error is small but always tends to make σ_{exp} less than the true value. The softening is of course due to the change in wave-length of the modified portion of the scattered x-rays. This suggests that, since we know the change of wave-length on scattering and therefore also the change in absorption coefficient of the modified x-rays on scattering, we can separate s_1 and s_2 at a given value of ϕ by transferring a certain thickness of absorbing material from a position P in the primary beam to a position Q in the scattered beam and observing either the intensity of the scattered x-rays if the intensity of the primary x-rays is kept constant or the change in the intensity of the primary rays necessary to keep the intensity of the scattered x-rays constant. In the present experiment the second alternative was used. Jauncey and DeFoe[6,14] have given formulas for determining the ratio $s_2/(s_1+s_2)$ for two cases. First, for the case in which the scattering block is placed in a position such that a normal to its face makes an angle $\theta=\phi/2$ with the forward direction of the primary beam, ϕ being the scattering angle, we have

$$s_2/(s_1+s_2)=\frac{y-1}{(y-1)+[(1-e^{-g})/ge^{-g}]e^{-(kd_1+b)}(1-ye^{-kd})}. \qquad (7)$$

Second, for the case in which the scattering block is set in such a position that the plane of its face bisects the scattering angle ϕ, we have

$$s_2/(s_1+s_2)=\frac{y-1}{(y-1)+Be^{-kd_1}(1-ye^{-kd})}. \qquad (8)$$

In the above equations the symbols used are defined as follows: $y=I_2/I_1$ where I_1 and I_2 are the intensities of the primary x-rays before and after the transfer of a thickness d of absorbing material from P to Q, the values of I_1 and I_2 being such that the intensity of the scattered rays is the same after the transfer as before; d_1 is the thickness of absorbing material at Q_1 which is not transferred (e. g. the thickness of the aluminum window of the ionization chamber); $k=(\mu_2-\mu_1)$; $b=(\mu_6-\mu_5)R+g$; $g=(\mu_4-\mu_3)t \sec \frac{1}{2}\phi$, where t is the thickness of the scattering block and ϕ is the angle of scattering; $B=$

[13] Sadler and Mesham, Phil. Mag. **24**, 138 (1912).
[14] Jauncey and DeFoe, Proc. Nat. Acad. Sci. **11**, 517 (1925).

$e^{-hR}/\{1+(\mu_4-\mu_3)/2\mu_3\}$; $h=(\mu_6-\mu_5)$; R is the distance from scattering block to ionization chamber window; μ_1 is the absorption coefficient of primary x-rays in absorbing material; μ_2 is the absorption coefficient of modified x-rays in absorbing material; μ_3 is the absorption coefficient of primary x-rays in scattering material; μ_4 is the absorption coefficient of modified x-rays in scattering material; μ_5 is the absorption coefficient of primary x-rays in air; and μ_6 is the absorption coefficient of modified x-rays in air.

The change in absorption coefficient $k=(\mu_2-\mu_1)$ may be determined, either by plotting the experimental value of μ for the particular absorbing substance used against λ and reading from the curve the two values of μ corresponding to λ_ϕ and λ_0, or by making use of the relation

$$\mu/\rho = \text{const}\times\lambda^3+\sigma/\rho \tag{9}$$

In the present experiments aluminum was used for the absorbing material which was transferred from P to Q and Hewlett[15] gives the constant for aluminum in Eq. (9) as 12.4. If Eq. (9) is differentiated with respect to λ we obtain $\delta(\mu/\rho)$. Since σ/ρ varies slowly with the the wave-length we can treat it as a constant. We then have for aluminum

$$(\mu_2-\mu_1)=100.6\lambda_0^2(\lambda_\phi-\lambda_0), \tag{10}$$

$(\lambda_\phi-\lambda_0)$ being given by Eq. (1).

3. Experimental Arrangement and Procedure

The equations giving the ratio $s_2/(s_1+s_2)$ suggest the use of a balance method. The experimental arrangement is shown in Figs. 1 and 2. Two primary beams 1 and 2 which are in the same vertical plane are taken from the x-ray tube R which was placed at an angle of approximately 45° with the plane containing the two beams so as to eliminate any effect due to polarization in the primary rays. These were passed through the two slits C and D. C was about one square centimeter in area and its size was fixed. D could be varied from zero to about two square centimeters in area. The area of D was measured to .01 mm² by means of a micrometer screw. Absorbing material was placed at P_1 and P_2. Aluminum was used for absorbing material because the fluorescent radiation of aluminum does not interfere and because aluminum can be obtained commercially in a much higher state of purity than any other suitable substance. The scattered beams 1′ and 2′ from AB after passing through the absorbing material at Q_1 and Q_2 entered separate ionization chambers. These ionization

[15] C. W. Hewlett, Phys. Rev. **17**, 284 (1921).

chambers were connected by a glass tube and methyl iodide introduced by means of evaporation from a reservoir. This kept the concentration of methyl iodide vapor the same in the two chambers. The outer electrodes of the two ionization chambers were respectively connected to the opposite poles of a battery giving 180 volts, the middle point of the battery being grounded. The inner electrodes of the chambers were connected to each other and to a Compton electrometer. If the intensities of the scattered rays entering the two chambers is the same the electrometer shows no deflection. In these experiments the same thickness of aluminum was first placed at P_1 and P_2 also the thickness at Q_1 was the same as at Q_2. A balance was then obtained by varying the slit C by means of the micrometer screw and the reading of the

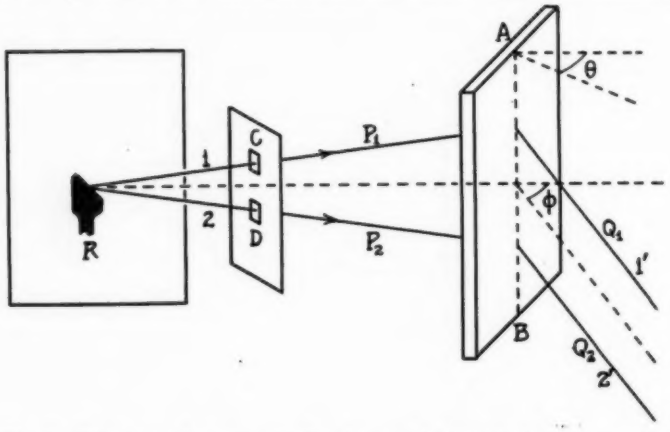


Fig. 1. Diagram of apparatus showing scattering block in the position of Method I, Eq. (7).

micrometer recorded. Second, a certain thickness of aluminum d was then transferred from P_1 to Q_1. In order to restore the balance it was then necessary to open the slit C by a definite amount. After the balance had been restored, the micrometer was again read. These two readings were taken as proportional to the intensities I_1 and I_2 in Eqs. (7) and (8). It remained necessary to find the wave-length of the x-rays used. This was done by opening the slit C to double its value when the amount of aluminum at P_1 and P_2 was equal, (the aluminum which was transferred from P_1 to Q_1 was replaced prior to this determination) then sufficient additional aluminum was placed at P_1 to restore a balance. From this added thickness, the average wave-length of the primary beam was calculated.

The electrometer used in determining the balance had a sensitivity of about 3000 to 5000 scale divisions per volt. All wires leading

to the electrometer were insulated by means of quartz and were placed inside grounded conductors. In this way it was possible to avoid insulation leaks and electrostatic fluctuations. A further precaution was taken to avoid any steady change in conditions which might occur during a set of observations by taking readings in groups of five. For example, let I_1 denote the micrometer reading when the aluminum was at P_1 and I_2 the reading at Q_1, then consider a group of five readings, say three of I_1 and two of I_2, in which case the first, third and fifth were of I_1 and the second and fourth of I_2 or vice versa. The average values of I_1 and I_2 were then determined and a value for $y=I_2/I_1$ calculated. Three such groups of readings were made for each angle in the case of any given wave-length and substance. The values of y so obtained were then averaged and the ratio calculated from this

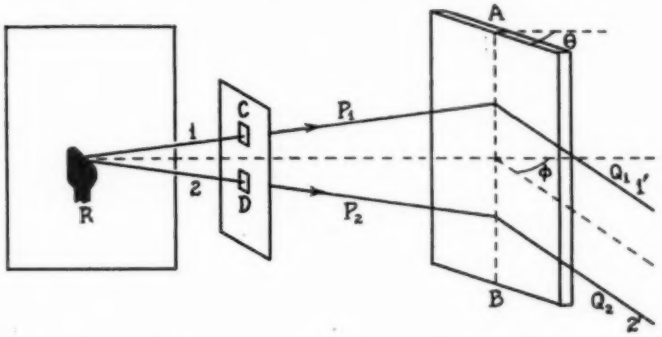


Fig. 2. Diagram of apparatus showing scattering block in the position of Method II, Eq. (8).

average value. Even with these precautions the error in some cases is probably as much as ten percent. The carbon block used was .5 cm thick and was placed in the position of Method I, Eq. (7), Fig. 1. For aluminum the position was the same but the thickness was reduced to .166 cm. In the case of copper the block was placed in the position of Method II, Eq. (8), Fig. 2, and was thick enough to absorb all the x-rays. The distance R of the block from the ionization chamber window was always 13 cm.

It should be mentioned that in the case of carbon it was necessary for the aluminum window of the ionization chamber to have a thickness of .045 cm in order to remove the characteristic rays of iron from the scattered beam. These characteristic rays were due to impurities in the carbon block. Calculations showed that a small percentage of iron as an impurity would entirely vitiate the results unless the window used was sufficiently thick to absorb all the characteristic radiation

of iron. The thickness used was known to be sufficient since it was the same as that used for copper, and previous tests had shown that this thickness was sufficient to reduce the characteristic radiation of copper to a negligible amount.

4. Results and Discussion

The experimental results for carbon, aluminum and copper are shown in Tables I, II, and III.

TABLE I
Carbon

ϕ	λ	y	d	d_1	$\frac{s_2}{s_1+s_2}$	$p(\phi)$	P_U/P_M
60	.345	1.047	.332	.045	.965	.977	1.1
60	.385	1.052	.322	.045	.857	.958	3.8
60	.435	1.052	.332	.045	.676	.920	5.5
60	.58	1.022	.083	.045	.623	.877	4.3
90	.325	1.087	.332	.045	.99	1.00	...
90	.475	1.192	.332	.045	.975	.980	1.3
90	.53	1.198	.332	.045	.82	.96	5.2
110	.31	1.109	.332	.045	1.00	1.00	...
110	.41	1.209	.332	.045	1.00	1.00	...
110	.45	1.222	.322	.045	.965	1.00	...
130	.33	1.157	.332	.045	1.00	1.00	...
130	.355	1.173	.322	.045	.975	1.00	...
130	.42	1.290	.332	.045	1.00	1.00	...

In these tables ϕ is the angle of scattering, λ the wave-length in angstroms, y the ratio I_2/I_1, d the thickness of the aluminum transferred. It is to be noted that the ratio $s_2/(s_1+s_2)$ is always less than

TABLE II
Aluminum

ϕ	λ	y	d	d_1	$\frac{s_2}{s_1+s_2}$	$p(\phi)$	P_U/P_M
90	.31	1.047	.332	.045	.67	.950	9.5
90	.36	1.065	.332	.045	.625	.939	9.0
90	.50	1.033	.083	.045	.537	.910	8.5
110	.30	1.079	.332	.045	.814	.965	6.1
110	.36	1.112	.332	.045	.783	.952	3.6
110	.50	1.051	.083	.045	.760	.920	5.0
130	.28	1.100	.332	.045	.926	.974	3.0
130	.33	1.134	.322	.045	.895	.964	3.1
130	.385	1.180	.332	.045	.865	.953	3.2

$p(\phi)$ except where each is equal to unity. This means that the probability P_U of an electron's scattering unmodified rays in a direction ϕ is always greater than the probability P_M of an electron's scattering modified rays. In the last columns of the tables are shown the ratio

of these two probabilities. There are several blanks in the last column where the value of P_U/P_M is indeterminate. It might be mentioned that Woo[16] also finds $s_2/(s_1+s_2)$ to be less than $p(\phi)$ for Mo$K\alpha$ x-rays scattered from various elements.

TABLE III

Copper

ϕ	λ	y	d	d_1	$\frac{s_2}{s_1+s_2}$	$p(\phi)$	P_U/P_M
90	.27	1.035	.332	.045	.62	.90	5.5
90	.32	1.049	.332	.045	.609	.79	5.1
90	.36	1.059	.332	.045	.58	.67	5.2
100	.27	1.050	.332	.045	.74	.923	4.2
100	.32	1.071	.332	.045	.73	.901	3.3
100	.36	1.083	.332	.045	.68	.884	3.6
100	.41	1.096	.332	.045	.63	.849	3.3
130	.27	1.093	.332	.045	.94	.948	1.2
130	.345	1.144	.332	.045	.89	.916	1.4
130	.48	1.061	.083	.045	.81	.867	1.5

Jauncey[7] has shown that the unmodified scattering should disappear at an angle and a wave-length such that $p(\phi)$ becomes unity. This occurs at a value of ϕ given by

$$\text{vers } \phi = (3+2\sqrt{2})(\lambda_0^2/\lambda_e)(mc/h) \tag{11}$$

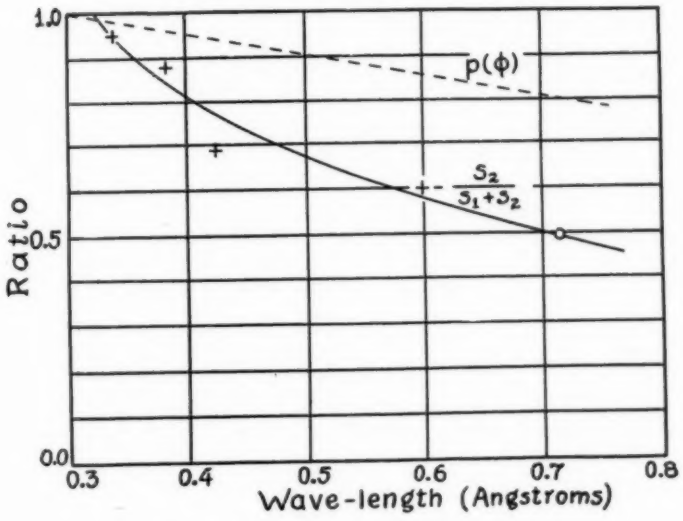


Fig. 3. Scattering from carbon at 60°.

A test of this formula has been made for scattering by carbon. The experimental values of $s_2/(s_1+s_2)$ are plotted against λ for the angles

[16] Y. H, Woo, Phys. Rev. **27**, 119 (1926).

60° and 90° and are shown as the full curves in Figs. 3 and 4 respectively. It is seen that $s_2/(s_1+s_2)$ becomes unity at wave-lengths of 0.32A and 0.46A for angles of 60° and 90° respectively. For carbon the K absorption limit is 47A and solving Eq. (11) at values of $\phi=60°$ and 90° we obtain $\lambda_0=.31$A and .44A respectively. These agree very well with the experimental values. In the case of carbon at $\phi=110°$ the solution of Eq. (11) for λ_0 is 0.51A. As all the wave-lengths examined were less than 0.51A the ratio $s_2/(s_1+s_2)$ is approximately 100 percent. It will be noted that experimental values of $s_2/(s_1+s_2)$ are shown in Figs. 3, 4 and 5 for $\lambda=0.71$A. These values are taken from results obtained by Woo[16] for the scattering of MoK x-rays by

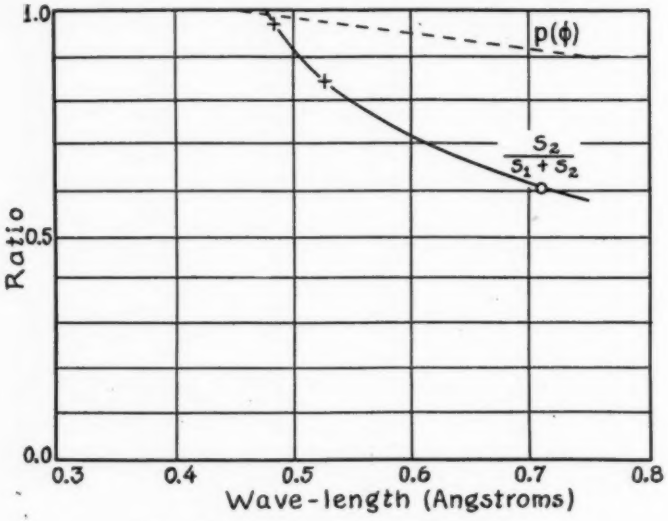


Fig. 4. Scattering from carbon at 90°.

carbon. It is seen that Woo's values fall upon the extrapolated portion of the curve as determined by the writer. The writer's values are therefore consistent with those of Woo. The broken curves in Figs. 3 and 4 are the graphs of $p(\phi)$ against λ for 60° and 90° respectively. It is seen that the curves for $s_2/(s_1+s_2)$ fall below the curves for $p(\phi)$ except where each becomes unity.

The smooth curves of Figs. 5 and 6 are the graphs of $s_2/(s_1+s_2)$ against λ for aluminum and copper at $\phi=90°$. These curves are not extrapolated to cut the 100 percent line because the amount of the extrapolation would be so large that the results would be of little value. We may however use the results for copper to test the truth of Eq. (4). The experimental value of (s_1+s_2) has been determined for copper at 90° and a wave-length of .4A. Interpolating the results

of Barkla and Dunlop[12] we find the value of (s_1+s_2) to be $1.40s_0$ where s_0 is the Thomson value at 90°. A similar determination by DeFoe and Jauncey[14] gives $(s_1+s_2)=1.24s_0$. The mean of these values

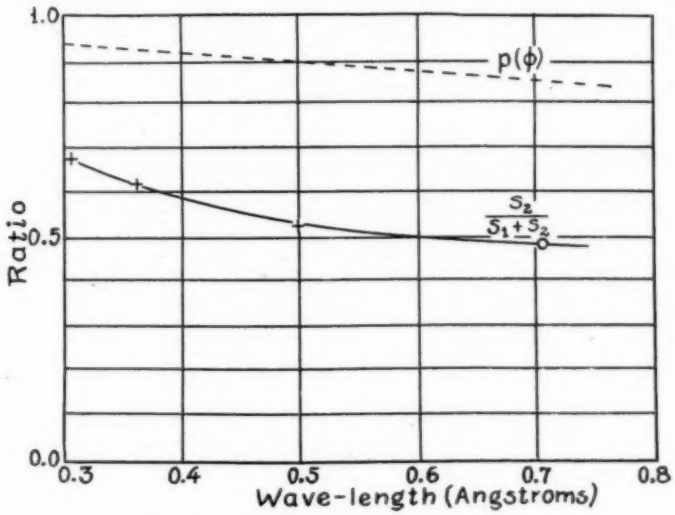


Fig. 5. Scattering from aluminum at 90°.

is $1.32s_0$. The experimental value of $s_2/(s_1+s_2)$ for $\lambda=0.4$A at $\phi=90°$ is from Fig. 6 found to be 0.54. Hence $s_2=0.54\times1.32s_0=0.71s_0$.

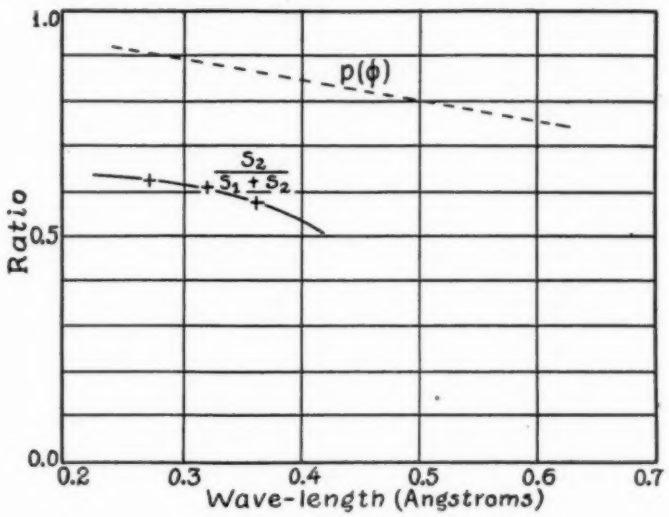


Fig. 6. Scattering from copper at 90°.

When unmodified rays are present the theoretical value of s_2 is given by Eq. (4). In the present case $p(\phi)$ has the numerical value of 0.85.

The value of the remainder of the right side of Eq. (4) is $0.87s_0$ for $\lambda=0.4$A. Hence $s_2=0.74s_0$ which agrees well with the experimental value $0.71s_0$. The use of s_1 is of course the difference between (s_1+s_2) and s_2 is therefore $0.58s_0$. It is unfortunate that more values of (s_1+s_2) are not available for various scattering substances, wave-lengths and angles of scattering for then we could arrive at a relation between s_1, λ and ϕ.

On examining the values of the ratio of P_U/P_M as given in the last columns of Tables I, II and III, we note a general tendency for the ratio for a given wave-length to become less as the angle increases. In fact in the case of copper the ratio seems to approach unity at an angle of about 130°. The results for carbon and aluminum are not quite so definite, but it must be remembered that the ratios, $s_2/(s_1+s_2)$, as given in the sixth column are not so accurate as could be desired and it might well be that the values of P_U/P_M even for carbon and aluminum approach unity for large angles. This approach to unity implies that the unmodified scattering per electron in a direction ϕ approaches the modified scattering per electron when ϕ becomes large.

The experimental results so far as they go support Jauncey's theory of the unmodified line in that the unmodified scattering disappears for a given angle at the wave-length demanded by the theory and also in that the experimental value of the modified scattering coefficient at 90° for copper is in agreement with the theoretical value.

In conclusion, the writer wishes to express his thanks to Professor G. E. M. Jauncey who suggested this problem, for his aid an interest in the carrying out of this research.

Washington University,
St. Louis, Mo.
March 2, 1926.

NOTE ON THE QUANTUM THEORY OF THE UNMODIFIED LINE IN THE COMPTON EFFECT

By G. E. M. Jauncey

Abstract

Disappearance of the unmodified line.—According to the theory developed in two previous papers (Phys. Rev. 25, 314 and 723) it is shown that the unmodified line should disappear at a scattering angle ϕ given by vers $\phi = (3+2\sqrt{2})(\lambda_0^3/\lambda_s)(mc/h)$ where λ_0 is the wave-length of the primary x-rays and λ_s the K critical absorption wave-length of the scattering substance. This formula shows that there is an unmodified line for all values of ϕ when Mo Kα rays are scattered by carbon and heavier elements, but when scattered by boron and lithium this line should disappear at 147° and 60° respectively.

Ratio of the energies in the modified and unmodified lines.—The theory of the previous papers gives the ratio of the number of electrons in orbital positions U such as to scatter unmodified rays in a direction ϕ to the number of electrons in orbital positions M such as to scatter modified rays. A formula for the ratio of the probability of an electron scattering when in the U position to that when in the M position is given together with a simpler method for calculating the number of electrons in the M position to the number in the U and M positions for elliptic orbits.

1. Disappearance of the Unmodified Line

In two previous papers,[1,2] the writer has explained the existence of the unmodified line in the Compton effect by showing that there is a certain range of positions of the scattering electron of a given type (K, L, etc.) in its Bohr orbit from which the electron cannot be ejected from the atom by the scattering process when x-rays are scattered at an angle ϕ with the direction of the primary rays. For convenience, we shall speak of an electron which is in an orbital position such that it cannot be ejected by the scattering process as being in the U position and of an electron which is in a position such that it can be ejected as being in the M position. Jauncey's theory requires that for scattering in a direction ϕ by a given type of electrons the ratio of the number N_M of electrons in the M position to the total number (N_U+N_M) of electrons in the U and N positions is approximately given by

$$\frac{N_M}{N_U+N_M} = \frac{\alpha_0 \text{ vers } \phi + 2\sqrt{2\alpha_s}\sin\tfrac{1}{2}\phi - \lambda_0/\lambda_s}{4\sqrt{2\alpha_s}\sin\tfrac{1}{2}\phi}, \qquad (1)$$

[1] G. E. M. Jauncey, Phys. Rev. **25**, 314 (1925).
[2] G. E. M. Jauncey, Phys. Rev. **25**, 723 (1925).

where λ_0 is the wave-length of the primary x-rays, λ_s is the critical absorption wave-length for the particular type of electrons under consideration, $\alpha_0 = h/mc\lambda_0$ and $\alpha_s = h/mc\lambda_s$. Eq. (1) is true for those types of electrons which move in circular orbits, while a more complicated formula[2] exists for electrons which move in elliptic orbits.

The ratio $N_M/(N_U+N_M)$ is to be taken as zero when the right side of Eq. (1) is negative and as unity when the right side is greater than unity. For values of the right side between zero and unity, the ratio increases as ϕ increases and as λ_s decreases. The ratio is therefore least for the K electrons. Hence when the ratio becomes unity for the K electrons, it will be unity for all the other electrons, and we shall have no unmodified line. Therefore, equating the right side of Eq. (1) to unity and solving for ϕ, we obtain the value of ϕ for which the unmodified line in the Compton effect should disappear. This value of ϕ is given by

$$\text{vers}\,\phi = (3+2\sqrt{2})(\lambda_0^2/\lambda_s)(mc/h) \qquad (2)$$

If λ_0 and λ_s are measured in angstroms, Eq. (2) may be written vers $\phi = 242(\lambda_0^2/\lambda_s)$. For the scattering of MoKα x-rays by the K electrons of carbon we have $\lambda_0 = 0.71$A and $\lambda_s = 47$A, so that the right side of Eq. (2) is greater than 2 and there is no real solution for ϕ. A similar result holds for the scattering of MoKβ x-rays by carbon. Hence there is an unmodified line for all values of ϕ when MoKα and MoKβ x-rays are scattered by carbon and elements of higher atomic number than carbon. However, for the K electrons of boron we have $\lambda_s = 66$A and there is now a real solution for ϕ. For scattering by boron the unmodified line should disappear at $\phi = 147°$, while the unmodified Kβ line should disappear at $\phi = 117°$.

Jauncey, Boyd and Nipper[3] have tested this experimentally by scattering MoK x-rays by boron at about 145° to 150°, the scattered spectrum being examined photographically by means of a Sieman-Ross x-ray spectrometer. The photograph showed the modified Kα and Kβ lines plainly but the unmodified lines were not apparent although in a comparison experiment where carbon was the scattering substance the unmodified lines were evident. As further experimental evidence Allison and Duane[4] and Woo[5] have scattered MoK x-rays from lithium at angles greater than 60° and find either very little or no evidence of the unmodified lines. For the K electrons of lithium $\lambda_s = 240$A, so that

[3] Jauncey, Boyd and Nipper, Phys. Rev. **27**, 103 (1926).
[4] Allison and Duane, Phys. Rev. **26**, 300 (1925).
[5] Y. H. Woo, Phys. Rev. **27**, 119 (1926).

the unmodified MoKα and Kβ lines should disappear at 60° and 53° respectively. It might be mentioned that the existence of the unmodified MoKα line might have been explained on the following assumptions: (1) the electrons are at rest in the atom, (2) the energy given to the electron by the scattering process is that given to a free electron, and (3) there is an unmodified line unless this energy is greater than the binding energy of the electrons. These assumptions give the condition vers $\phi=(\lambda_0^2/\lambda_s)(mc/h)$ for the disappearance of the unmodified line, which in the case of carbon should be at 75°. Experimentally, however, the unmodified MoKα line does not disappear at any angle when the x-rays are scattered from carbon. We are therefore left with the theory of the unmodified line as developed by Jauncey[1] as being the only available explanation.

2. Ratio of the Energies in the Modified and Unmodified Lines

Jauncey and DeFoe[6] have shown that the assumption that the chance P_U that an electron will scatter in the direction ϕ when in the U position is equal to the chance P_M that an electron will scatter when in the M position is not necessary to Jauncey's theory of the unmodified line. Experiments show that P_U is greater than P_M and we are able to calculate the ratio P_U/P_M from experimental data. Eq. (1) gives the ratio $N_M/(N_U+N_M)$ for a given type (K, L etc.) of scattering electrons so long as these electrons are moving in circular orbits. If, however, the electrons are moving in elliptic orbits the method of calculation is as follows: Referring to Fig. 1 the curves $ABCD$ and $DEFG$ are taken from Fig. 3 in Jauncey's paper.[2] The curve $ABCD$ is for circular orbits while the curve $DEFG$ is representative of the curves for elliptic orbits. If the line AD is divided at L in the ratio LD/AD such that this ratio is given by the right side of Eq. (1) and the line LM is drawn perpendicular to AD then the ratio $N_M/(N_U+N_M)$ for the particular type of electrons under consideration is given by the ratio of the area $LMFGK$ to the area $HDEFGK$. The weighted mean of the ratios $N_M/(N_U+N_M)$ for the various types of electrons is represented by $p(\phi)$. If now s_1 and s_2 represent the unmodified and modified scattering coefficients per unit solid angle in the direction ϕ, then the ratio s_2/s_1 can be found experimentally by the methods of Woo[5] and DeFoe.[7] We then have

$$P_U/P_M=(s_1/s_2)\cdot p(\phi)/\{1-p(\phi)\} \tag{3}$$

[6] Jauncey and DeFoe, Phil. Mag. **1**, 711 (1926).
[7] O. K. DeFoe, Phys. Rev. **27**, 675 (1926).

Woo in a recent paper[5] finds the ratio s_2/s_1 by obtaining the spectrum of scattered MoKα x-rays and comparing the areas under the modified and unmodified humps in his curves. Woo finds s_2/s_1 for carbon at 90° to be 1.45. However Woo compares this with a value 1.74 for the ratio of the 'intensities' calculated on theoretical grounds in a paper by the writer.[2] In this paper[2] the writer distinguishes between 'intensity' and 'energy.' In the sense in which the writer has used the words, Woo has measured the ratio of the 'energies.' The writer has used the word 'intensity' to denote the height of the ordinate of the most intense part of the modified or unmodified hump and not the area under the hump; while the word 'energy' implies the area. Ac-

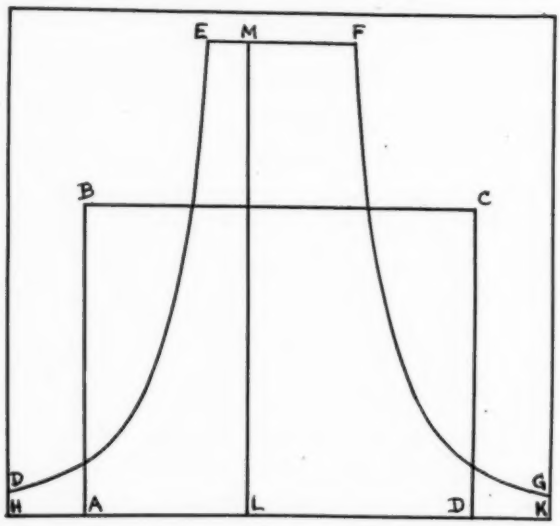


Fig. 1. Curves for obtaining the ratio $N_M/(N_U+N_M)$ for elliptic orbits.

cording to the argument of the paper[2] the ratio of the 'energies' for MoKα x-rays scattered at 90° by carbon is 10.9 and by sulfur is 4.2. These values, however, are based on the assumption that $P_U=P_M$. As s_2/s_1 is quite evidently smaller than the ratio of the 'energies,' we see that P_U is greater than P_M and from Eq. (3) the ratio P_U/P_M for MoKα x-rays scattered by carbon at 90° is $10.9/1.45=7.5$. Thus we see that scattering is about 7.5 times as probable when the electron is in the U position as in the M position. It should be remarked that Eq. (3) gives only the mean value of P_U/P_M. It might well be that this ratio has different values for the different orbits.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.
March 3, 1926.

THE REFRACTION OF X-RAYS IN PRISMS OF VARIOUS MATERIALS

By C. M. Slack

Abstract

The method consisted in the use of the "double x-ray spectrometer" for measuring the extremely small changes in angle produced by refraction in prisms, which were placed between two crystals. The rocking curves from the second crystal were from 6 to 10 seconds of arc wide at half maximum and, under favorable temperature conditions, a shift of .2 seconds could be detected. Two different wave-lengths of x-rays and prisms of various materials were used. The values of $\delta \times 10^6$, where $\delta = 1 - \mu$, are as follows:

λ	silver	copper	sulfur	aluminum	carbon	celluloid	paraffin
.7078A	5.85±.3	5.95±.5	1.39±.05	1.68±.07	1.23±.15	.980±.03	.701±.03
1.537 A				8.40±.2		4.78 ±.1	3.28 ±.15

These results agree with the Lorentz dispersion formula within experimental error. In the case of certain materials, notably graphite, the curves from the second crystal were extremely broad (20 to 50 seconds), caused by internal refraction due to the granular structure. This seems of interest with respect to the possibility of comparing internal arrangements of particles in various samples, though nothing of that sort was attempted here.

Introduction

In a recent paper by Bergen Davis and C. M. Slack[1] a method was described which employed the "double x-ray spectrometer"[2] for the measurement of the refraction of x-radiation in an aluminum prism. The present paper presents a continuation of that work using a variety of substances as prisms.

Experimental Method

In all cases, except copper, silver and carbon, *double* prisms were used, in which the ray passed through the prism symmetrically, being bent the same at each surface. With copper and silver the difficulty experienced in perfecting the prism edge was overcome by backing a carefully polished face of the material against a steel plate and then milling the other face to the angle desired. The ray was then allowed to enter normally, refraction taking place on emergence. In these metals, on account of the high absorption, it was not possible to work at a distance greater than .01 cm from the edge. With carbon a right angled block was used, this being rotated to obtain the refracting angle.

[1] Bergen Davis and C. M. Slack, Phys. Rev. 27, 18 (Jan., 1926).

[2] Bergen Davis and W. M. Stempel, Phys. Rev. 17, 608 (May, 1921).

In measuring the refraction, the first crystal was set for the wavelength desired (MoKα or CuKα) and a direct rocking curve from the second crystal was taken. Then the prism was inserted and the rocking curve again taken. The shift in the peak measured the bending of the ray in the prism. This process was usually repeated several times at different prism positions to make sure that the prism was across the x-ray beam and to iron out slight irregularities in the prism surfaces and the larger shifts due to temperature changes.

In calculating δ from the prism angle and the measured bending a simple modification of the formula for the refractive index of a material for light was used:

$$\delta = -\theta \cot R \tag{1}$$

for single prism:

$$\delta = -\tfrac{1}{2}\theta \cot \tfrac{1}{2} R \tag{2}$$

for double prism. R is the prism angle and θ the deviation of the ray. The sign of θ is negative for bending as observed, which gives a positive value for δ in every case.

Results and Discussion

The results are shown in Table I.

TABLE I

Data on refraction of x-rays. Values of δ $(= 1-\mu)$.

Substance	prism angle	(degrees)	refraction (sec. of arc)	$\delta\times10^6$ observed	$\delta\times10^6$ Calc. by Lorentz formula complete	omitting char. freq.
			.7078A			
silver	single	63.5	2.42±0.1	5.85 ±0.3	5.80	6.33
copper	single	60.0	2.12±0.2	5.95 ±0.5	5.72	5.60
sulfur	double	168.3	5.39±0.2	1.39 ±0.05	1.37	1.37
aluminum	double	166.0	5.62±0.2	1.68 ±0.07	1.77	1.77
carbon	single	86.4	4.02±0.5	1.23 ±0.15	1.10	1.10
celluloid	double	171.0	5.12±0.1	.980±0.03	.991	.991
paraffin	double	173.0	4.71±0.15	.701±0.03	.714	.714
			$\lambda=1.537$A			
aluminum	double	116.0	5.53±0.1	8.40 ±0.2	8.46	8.44
celluloid	double	144.0	6.06±0.1	4.78 ±0.1	4.71	4.71
paraffin	double	152.0	5.40±0.15	3.28 ±0.15	3.37	3.37

The first of the last two columns was obtained from a modification of the Lorentz dispersion formula[3] thus:

[3] R. von Nardroff, Phys. Rev. **24**, 143 (1924).

$$\delta = \frac{e^2}{2\pi m}\left[\frac{n_1}{\nu^2 - \nu_c^2} + \frac{n_2}{\nu^2}\right] \tag{3}$$

where ν_c is the critical absorption frequency for the K series.

Which for the last column was simplified to

$$\delta = \frac{e^2}{2\pi m}\,\frac{n}{\nu^2} \tag{4}$$

It will be observed that only in the cases of silver and copper did the consideration of ν_c have an appreciable effect and in these it brought the result nearer the experimental value.

The curves were extremely narrow and of almost perfect regularity. It seems of interest to note that, with the exception of a few cases mentioned below, the transmission curve had practically the same width as the direct. The peak of an individual curve could be located to within .2 seconds. A shift due to temperature caused considerable trouble, but as it affected both curves alike it could be largely eliminated by a series of "out" and "in" curves. The other errors, such as lining up of the prism in mounting, measuring of prism angle, imperfections in prisms, etc., were not so easy to determine but in no case would introduce an error greater than .2 seconds, and in most cases considerably less. The discrepancy in the case of carbon is due to curve broadening discussed below.

Fig. 1 is a direct curve which shows the accuracy with which the peak can be located under favorable conditions. It also shows to a fine degree the perfect structure of the crystals used.

Because of the relatively low absorption in celluloid and the high accuracy with which it was possible to mill the prism edge, quite large refractions could be obtained. Fig. 2 shows such a case. The prism was pushed only part way across the beam, (a) representing that which passed the edge and (b) the portion which was refracted in the prism.

Internal Refraction in Graphite

In the determination of δ for carbon a piece of brush graphite kindly supplied by Dr. Welsh of the Union Carbide and Carbon Research Laboratories was used. It was observed immediately that the curves, instead of being 6 seconds wide at the half maximum, were of the order of 30 to 50 seconds, depending on the prism position. This effect apparently came from internal refraction due to the granular structure of the material. To check this, however, the transmission through a paraffin block was compared with that through the same amount granulated and it was found that the curve width was nearly doubled for the granulated material. There was some broadening in the case of

sulfur, due to the same cause. In no case was the effect noticed where it could be attributed to the surface conditions though in every case surface irregularities were enormous as compared to the x-ray wavelength.

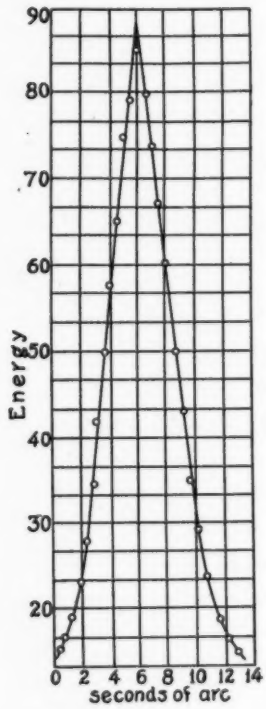


Fig. 1. Apparatus curve.

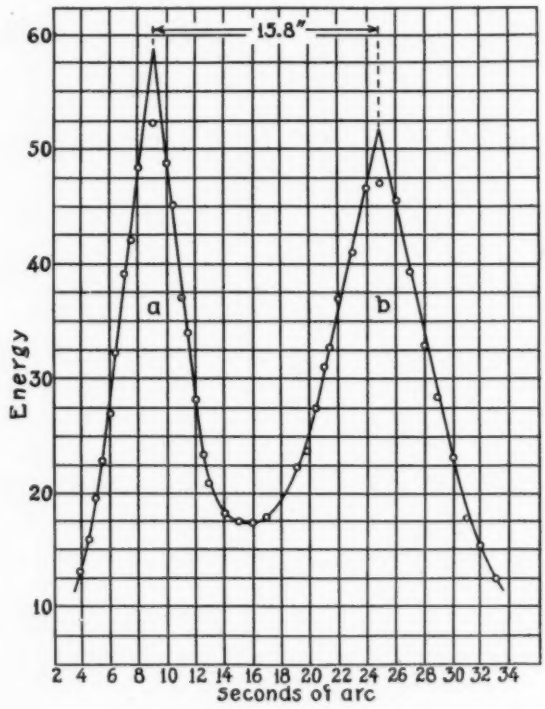


Fig. 2. Refraction in celluloid.

An investigation was made of the transmission through graphite strips of different thickness and the results obtained are given in Table II.

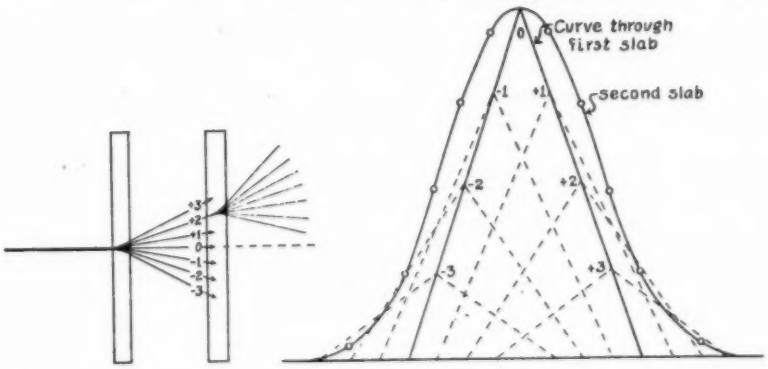
TABLE II

Data on the broadening of refraction curves in graphite.

Thickness of graphite	Curve width at half max.	Broadening	
	MoKα		
13.8 mm	58 sec.	52 sec.	±5
8.4	46	40	±5
4.3	30	24	±3
2.2	19	13	±3
1.2	15	9	±2
.62	10	4	±2
0.	6	0	...
	CuKα		
1.2	58	47	±5
.62	45	34	±4
0.	10.8	0	...

This variation of the broadening with thickness may be explained as follows. Consider the original beam as plane parallel and that in traversing a slab of known thickness it is divided into a large number of smaller elements (see Fig. 3) angularly dispersed in a manner which can be determined from a corresponding rocking curve. On traversing a second slab of equal thickness each of these small elements will be angularly dispersed in a manner exactly as was the original beam through the first slab. The total effect is then to be obtained by summation over all the elements.

The numerical value of the intensity at any angle is obtained experimentally as the height of that particular ordinate on the rocking curve. Thus to obtain the broadening graphically, curves were drawn, having the same distribution as the original, from a number of points



Figs. 3 and 4. Diagrams to illustrate how the internal refraction of x-rays in graphite broadens the rocking curves.

on the original. Then the ordinates of the elementary curves were added and the scale reduced for comparison. (See Fig. 4). This gave a curve showing distribution of intensity after traversing a second unit slab. This process was repeated for each thickness. In practice some eight points were taken on each curve and the check with the experimental results was within the error of observation. To explain quantitatively the original broadening would demand a knowledge of the shape, size and distribution of the carbon particles, which is not available.

In conclusion I wish to express my appreciation to the members of the Physics Department for their cooperation in this work, and especially to Professor Davis for the suggestion of the problem and his constant aid in overcoming difficulties encountered.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
January 7, 1926.

THE ORIGIN OF K-RADIATION FROM THE TARGET OF AN X-RAY TUBE

By Mark Balderston

Abstract

The fluorescent energy transformation coefficient, the ratio of the energy of secondary K-radiation emitted by an elementary volume of the radiator to the energy absorbed by it from the exciting x-rays, is observed for Fe, Ni, Cu, Zn, Mo, and Ag. The ratio of quanta emitted as K-radiation to quanta absorbed seems to be a constant for a given metal; Fe—33 percent; Ni—39 percent; Cu—43.5 percent; Zn—50 percent; Mo—83 percent; Ag—75 percent. Making use of the experimentally determined values of the transformation coefficient the *fluorescent K-characteristic radiation* from the target of an x-ray tube is calculated for Cu and Ag, and compared with observed values of the total K-radiation. An estimate is also made from theoretical considerations of the relative amounts of direct impact K-characteristic radiation to be expected from an x-ray tube target. The calculations indicate that for silver and probably for other elements of high atomic number practically all of of the K-characteristic radiation from an x-ray tube is fluorescent in origin while for copper and probably other elements of low atomic number a considerable part of the K-radiation is due to direct impact of the cathode electrons.

FOLLOWING the discovery by Kaye[1] that characteristic x-radiation was emitted by the target of an x-ray tube Barkla[2] explained the phenomenon as secondary radiation resulting from the absorption, in the target itself, of the general radiation. Beatty[3] examined the subject theoretically, not however publishing his method of analysis, and announced that not over ten per cent of the observed characteristic radiation could be so accounted for. An experimental investigation conducted with as much care as was possible with the facilities then available (1912) convinced him that practically all of the K-radiation from an x-ray tube target was the result of direct impact of the cathode electrons without the intermediate formation and absorption of general x-radiation.

With the x-radiation spectrometer came new evidence for Barkla's theory in the form of a sharp discontinuity in the general radiation spectrum at what was soon recognized as the K-absorption limit. Apparently the wave-lengths below the K-limit were strongly absorbed

[1] G. W. C. Kaye, Phil. Trans. **A209**, 123–151 (1909).
[2] C. G. Barkla and C. A. Sadler, Phil. Mag. **17**, 739–760 (1909).
[3] R. T. Beatty, Proc. Roy. Soc. **87**, 511–518 (1912).

in the target and it was but natural to assume that the K-radiation was an indirect effect resulting from this absorbed energy. Under the influence of Beatty's work, however, this evidence was largely discounted and explained as due to absorption by small bumps on the face of the target. It seems to have been generally assumed that if the target were absolutely smooth there would be no such discontinuity; that the characteristic radiation would appear as a new effect superposed on the general radiation. Beatty's[3] investigation of the total radiation from a copper target added weight to these conclusions; for as the velocity of the impinging electrons was increased the intensity of the resulting x-rays increased being nearly proportional to the fourth power of the velocity until the K-radiation appeared when the rate of increase became more rapid as though a new effect were superposed on the old. A similar piece of work by Brainin[4] confirmed Beatty's result for copper and secured similar results for cobalt, palladium and platinum. Molybdenum, however, gave a perfectly straight line showing no break at the K-absorption limit while silver showed a well defined decrease in efficiency at about the voltage corresponding to the K-absorption limit.

Meanwhile D. L. Webster and A. E. Hennings[5] have shown that for a molybdenum target, the focal spot of which had been fused so that there could not possibly be inequalities great enough to explain any discontinuity in the general radiation curve, nevertheless a well defined discontinuity appeared which they explained as wholly due to K-absorption in the target and from the amount of the discontinuity calculated the mean depth of production of the x-rays at the K-absorption limit. Their result is well in accord with the data on penetration of electrons found by Terrill.[6]

These results make it seem worth while to redetermine on the basis of present knowledge the amount of fluorescent or indirect K-radiation to be expected from the target of an x-ray tube. Our knowledge of absorption coefficients is adequate. The results of Terrill's work on electron penetration in metals gives at least a rough indication of the mean depth of production of general x-radiation of a given wave-length. Webster and Hennings' work mentioned above indicates its reliability. There remains to find what we have termed the "fluorescent transformation coefficient," ϕ, for a given range of wave-length of incident x-rays; i. e., the ratio of the energy of fluorescent

[4] C. I. Brainin, Phys. Rev. **10**, 461 (1917).
[5] D. L. Webster and A. E. Hennings, Phys. Rev. **21**, 301–311 (1923).
[6] H. M. Terrill, Phys. Rev. **22**, 101–108 (1923).

K-radiation from a small element of the target to the total energy absorbed by the element during the same time. The determination of this coefficient for a number of metals ranging from iron (26) to silver (47) and for a number of wave-lengths from .314Å to .9Å was the object of the investigation of which this paper is a report.

Apparatus and Experimental Method

The apparatus is an x-ray spectrometer with calcite crystal *C* (Fig. 1) and a 15 cm ionization chamber *A*, containing air saturated

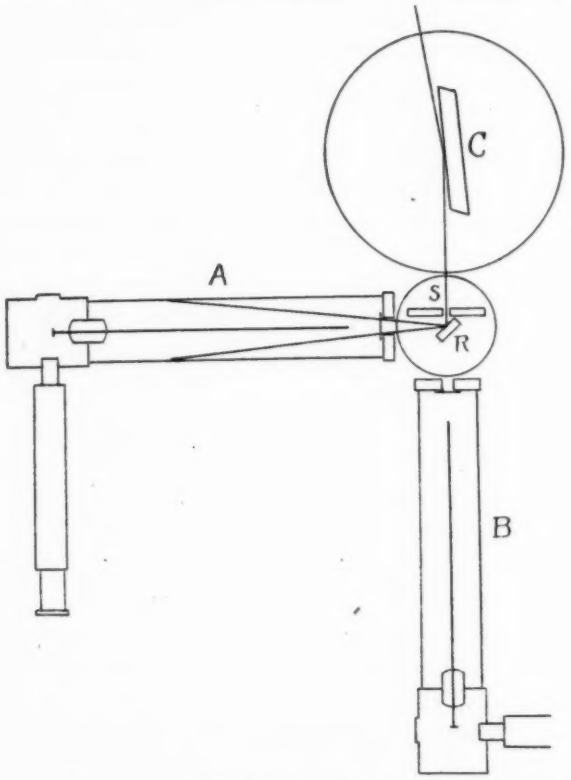


Fig. 1. Apparatus. *C* represents the calcite crystal, *A* and *B* the two positions of the movable ionization chamber, *R* the radiator, *S* the slit.

with ethyl bromide vapor. The chamber is mounted so that it may be revolved about a vertical axis 2 cm in front of the aluminum window making it possible to use the same chamber for measuring the secondary radiation from the specimen *R* and when turned through an angle of 90° to position *B*, the exciting radiation (*R* being then removed). The face of the radiator *R* makes an angle of 45° with the incident

beam so that the path of the incident x-rays in the radiator is equal to the mean path of the resulting characteristic radiation which reaches the ionization chamber. (On account of the very large solid angle subtended by the window this condition is only approximately satisfied.) The ionization current is measured by the rate of collapse of a small gold leaf electroscope mounted on the end of the chamber. The insulated electrode and the gold leaf are charged to a potential of about 60 volts. The sensitivity of the electroscope is about five divisions per volt and as the capacity is small the sensitivity per unit charge is high. The source of x-rays is a water-cooled tungsten-target tube of the Coolidge type. This tube was kindly constructed for the Laboratories by the Research Department of the Westinghouse Lamp Company. The source of power was a 500 cycle voltage rectified by two kenotrons and smoothed out by a large condenser.

The tube voltage and current were adjusted to suitable values. The crystal table was set at the proper angle to reflect the wave-length desired and, with the ionization chamber in position *B* (see Fig. 1) the proper position of the slit *S* was determined. The ionization current was then taken several times in this position giving a good mean value as a measure of the incident or exciting radiation. The chamber was then turned to position *A* at right angles to position *B*. With the tube input maintained at the same value there were then taken in turn; first, the natural leak of the electroscope and chamber; second, the ionization current with the required radiator *R*, placed in position; third, the natural leak again (the radiator *R* having been removed). This was repeated many times during a run, using different radiators. Occasionally during a run the incident radiation measurement was repeated as there was usually a slight drift in sensitivity due to change in temperature. The leak varied capriciously. Not over ten percent of it was due to stray x-rays (except at the highest voltages used) as was readily determined by shutting off the power. The amount of the leak varied a great deal with the weather but the range of variation during a given run was no greater in summer than in late winter. It was found necessary to keep the electroscope system charged throughout a run. If it were allowed to become completely discharged, for even a few seconds, it would give abnormally high values for a considerable period, the effect disappearing logarithmically with the time. Extreme precautions were taken to return the ionization chamber to exactly the original position after a reading of the incident radiation.

The ratio of the ionization current due to the secondary radiation (corrected for leak) to the ionization current due to the incident radiation is given in Table I.

TABLE I

Ratio of the ionization currents due to secondary and incident radiations.

Incident Wave-length	Value of c'/c for Ag	Mo	Zn	Cu	Ni	Fe
.306Å	.0093	.0058	.....	.00015	.....	.....
.359	.00826	.00653	.00065	.00052	.....	.....
.466	.00736	.00637	.00115	.00109	.00067	.00057
.571	.....	.0065	.00127	.00119	.00096	.00063
.678	.....	.....	.00195	.00171	.00138	.00094
.782	.....	.....	.00233	.00204	.00158	.00125
.887	.....	.....	.00297	.00256	.00230	.00161

ENERGY TRANSFORMATION COEFFICIENT, ϕ

In order to compare the vaues of the t ansformation coefficients of molybdenum and silver with those of the lighter elements, the radiations from which do not excite the K-radiation in bromine of the ethyl bromide, it is necessary to reduce the ratio of ionization currents given in Table I to the ratio which would have been obtained if the radiation could have been completely absorbed in air. This was done by making use of Barkla's[7] data on relative ionization in air and ethyl bromide. On account of the difference in path in the ionization chamber of different pencils of the divergent beam of K-radiation it was necessary to integrate over the solid angle ω to get the correction factor A′ for the K-radiation. The energy transformation coefficient ϕ, the fraction of energy absorbed by a small elementary volume of the radiator which is re-emitted as K-radiation is given by the following expression

$$\phi = \frac{4\pi}{\omega}\left[M\int_0^{t\sec\pi/4} \mu e^{-\mu x} e^{-\mu_K a x} dx\right]^{-1} A'c'/Ac\,.$$

The integral accounts for absorption in the radiator of the exciting radiation before transformation and for absorption of the resulting K-radiation before emergence from the radiator. ω is the solid angle subtended at the radiator by the window of the ionization chamber. μ is the coefficient of absorption of the radiator for the exciting radiation. μ_K is the coefficient of absorption of the radiator for its own K-radiation. $A'c'$ is the total energy per second of K-radiation entering the ionization chamber, expressed in terms of the total ionization it can produce in air. Ac is the energy per second of the exciting radia-

[7] C. G. Barkla, Phil. Mag. **20**, 372 (1910).

tion falling on the radiator, expressed in the same terms. M is a correction factor for absorption of the K-radiation in air and in the aluminum window of the ionization chamber. t is the thickness of the radiator. x is the path in the radiator of the exciting radiation before transformation. ax is the path in the radiator of the resulting K-radiation before emergence.

The ratio c'/c is given in Table I. The value of ω is $.030 \pm .004$. This is probably by far the least accurate factor entering into the determination of ϕ. The values of μ are from data of Richtmyer[8] and Hewlett.[9] Those of μ_K are from tables compiled by Ledoux-Lebard and Dauvillier.[10]

The amount of scattered radiation from the radiator entering the ionization chamber in position A is negligible. This is because of the fact that the coefficient of scattering is least at this angle (90°)[11] and that the shortness of the ionization chamber makes it relatively much more sensitive to the K-radiation than to the scattered radiations at the short wave-lengths. (It is only at short wave-lengths that the scattered radiation becomes important.)

The experimental values of ϕ are given in Table II below.

TABLE II

Values of ϕ, the ratio between the energy re-emitted as K-radiation by an elementary portion of the radiator to the energy absorbed by that portion from the incident or exciting x-radiation; and the values of the quantum transformation coefficient, u.

Wave-length of incident x-radiation	Values of ϕ for Ag	Mo	Zn	Cu[12]	Ni	Fe
.306Å	.398	.264	....	.021	....	....
.359	.414	.323	.077	.066	....	....
.466	.611	.488	.160	.156	.090	.086
.571	....	.632	.166	.163	.121.	.089
.678	....	....	.220	.193	.142	.103
.782	....	....	.251	.218	.153	.124
.887	....	....	.311	.263	.210	.148
Values of u	.75	.83	.50	.435	.39	.33

THE QUANTUM TRANSFORMATION COEFFICIENT, u

If now we plot ϕ versus λ, the wave-length of the incident x-radiation we find the relationship is apparently linear and the curves cut the

[8] F. K. Richtmyer, Phys. Rev. **18,** 13 (1921).

[9] C. W. Hewlett, Phys. Rev. **17,** 292 (1920).

[10] R. Ledoux-Lebard et A. Dauvillier, La Physique des Rayons X. Paris (1921).

[11] Barkla and Ayers, Phil. Mag. **21,** 270–278.

[12] At .385A G. E. M. Jauncey and O. K. DeFoe have found by a different method a single value of ϕ (for Cu) = .20 Proc. Natl. Acad. Sci. **11,** 520–2 (1925).

horizontal axis at points in the neighborhood of the origin. This suggests the possibility that the ratio of the number of quanta transformed to the total number of quanta absorbed is the same for a given radiator at all frequencies and that the decrease in ϕ with increase in frequency of the absorbed radiation is due to the increase, with frequency, in the energy of the absorbed quantum while the energy of the re-emitted quantum remains unchanged. The failure of the curves to pass through the origin may then be ascribed to lack of perfect proportionality between the calculated ionization and the energy of the radiation. If,

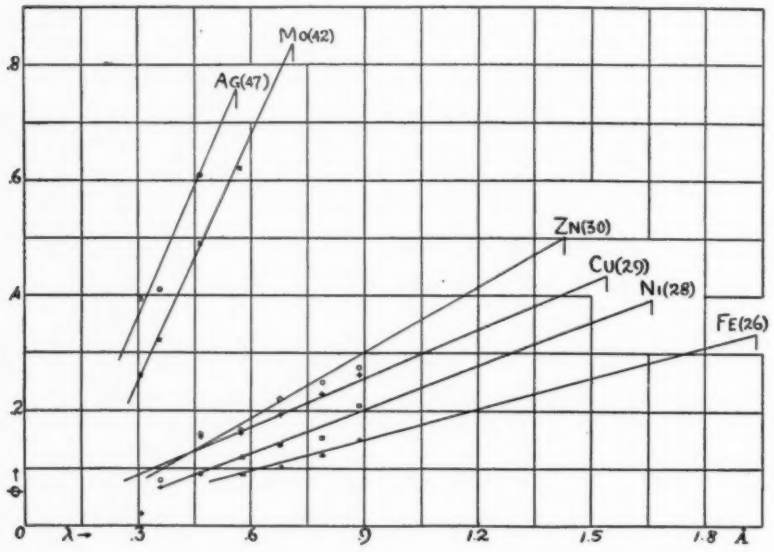


Fig. 2. Relation between ϕ and the wave-length of general x-radiation absorbed by the specimen.

$$\phi = \frac{\text{Energy of K-radiation emitted}}{\text{Energy of general x-radiation absorbed}}$$

now, the line be extended to the wave-length of the K-characteristic radiation it will represent an imaginary condition in which the absorbed quantum is equal to the re-emitted quantum and in consequence the ratio of the energy absorbed to the energy emitted will be equal to the ratio of the quanta absorbed to the quanta emitted. This quantity, u, has been derived from each of the curves in Fig. 2 and the values are shown in the last column of Table II.

The values of u have been plotted against the atomic number of the element in Fig. 3. Since the K-absorption, for any given wave-length according to the formulas given by Richtmyer[8] for absorption coefficients above and below the K-limit, is about 87 percent of the total

absorption, we should expect 87 percent of the absorbed quanta to eject K-electrons and in consequence the same number of quanta of K-radiation to be re-emitted, i.e., u should by this reasoning be equal to .87. The author's results, however, are in agreement with determinations of u by Barkla[13] and by Kossel[14] from data by Sadler.[15] These have been indicated on Fig. 3 where the author's values appear as circles, Barkla's as squares and Kossel's as crosses. Moreover, as indicated near the close of the paper in the determination of the

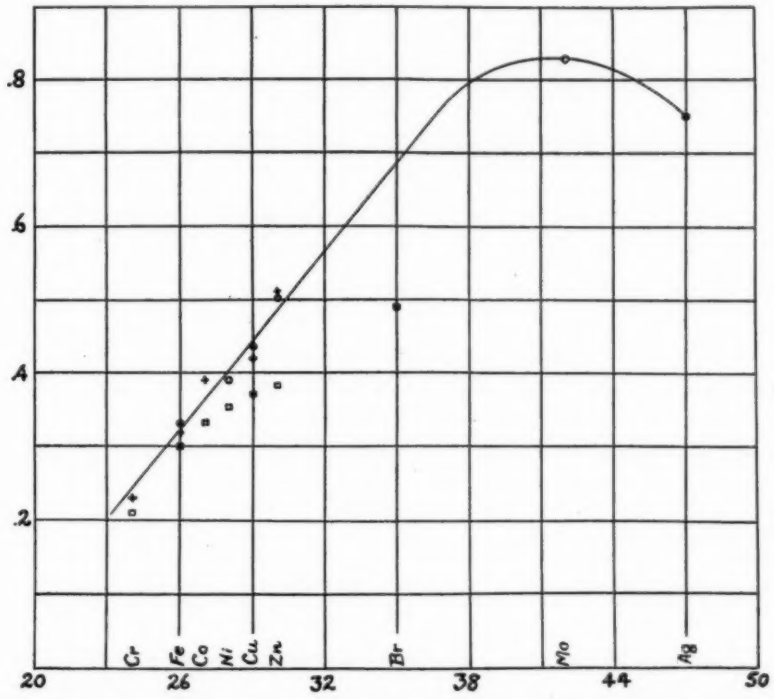


Fig. 3. Relation between ratio of quanta absorbed to quanta re-emitted and atomic number of element absorbing general x-radiation.

fluorescent K-radiation from the target of an x-ray tube and also of direct impact K-characteristic radiation, the use of values of ϕ based on $u=.87$ leads to an amount of fluorescent K-radiation hard to reconcile with experimental data while the use of the observed values of ϕ gives very satisfactory agreement. This points to the possibility that, at least for metals of low atomic number, only one half or less of the absorbed energy goes into photo-electric ejection of K-electrons,

[13] C. G. Barkla, Phil. Trans. **A217**, 315–360 (1918).
[14] W. Kossel, Zeits. f. Physik **19**, 333–346 (1923).
[15] C. A. Sadler, Phil. Mag. **18**, 107–132 (1909).

or else that these electrons are replaced by some process which does not involve the expected K-radiation. In this connection attention is called to the recent work of Auger[16] and of Bothe[17] indicating a "special inner absorption" of K-radiation by the parent atom, an absorption much more intense than the normal absorption by the substance, the energy leaving the atom in the form of a second ejected electron.

Determination of Indirect K-Characteristic Radiation from the Target

Unnewehr[18] has given some data on the ratio of the intensity of K-radiation to general radiation from the target of an x-ray tube. From a copper target at 15,400 volts the ratio between the energy of the Kα-radiation entering the ionization chamber of a simple Bragg form x-ray spectroscope and the energy of the general radiation entering simultaneously he finds to be 11.2. For a silver target at 36,400 volts he finds this ratio to be 2.7. We are now in a position to determine from fairly reliable data the ratio between the energy of indirect or fluorescent Kα-radiation entering the ionization chamber and the energy of the general radiation entering simultaneously. By comparing the two ratios we may then determine what part of the Kα-radiation measured by Unnewehr was fluorescent in origin, i. e., energy re-emitted by atoms of the target which have lost K-electrons by absorption of general x-radiation from other portions of the target. We will assume a general radiation curve I *vs* λ where, per unit volume of the target, I is the energy radiated having wave-length within a given range λ to $\lambda+\Delta\lambda$. We will further assume the mean depth of production of I to be given by the Whiddington law of electronic penetration—the depth at which the electron will have the same energy as the mean energy of the quantum of I. Since an error of 50 percent in the assumed depth of production will make a difference of only about 5 percent in the corresponding value determined for the fluorescent radiation this assumption of mean depth of production though not exact will certainly not cause a very large error in our results. The values of the penetration coefficients determined by Terrill[6] were used in the following work. It is now a simple matter to set up an expression for the energy of general radiation in a given wave-length range λ to $\lambda+\Delta\lambda$ from one elementary volume, $d\tau$, of the target which is absorbed in another element $d\tau.'$ Multiplying this value by ϕ, the fluorescent energy

[16] P. Auger, Comptes Rendus **180**, 65–68 (1925).
[17] Von W. Bothe, Phys. Zeits. **26**, 410–412 (1925).
[18] E. C. Unnewehr, Phys. Rev. **22**, 529–538 (1923).

transformation coefficient from the curve of Fig. 2 gives the resulting fluorescent K-radiation from the second element, $d\tau.'$ A portion of the resulting radiation lies within the very small solid angle $\delta'\omega$ necessary for reflection from the crystal—this quantity must then be corrected for absorption in reaching the surface of the target. A further correction factor R for absorption in air, reflection coefficient of the crystal, incomplete absorption in the ionization chamber, etc., is introduced. Its exact form is immaterial since identical corrections will apply to the general radiation entering the chamber with the K-radiation. It remains to integrate $d\tau'$ over that part of the target which contributes K-radiation to the beam reflected by the crystal and $d\tau$ over the layer of the target in which the general radiation of range λ to $\lambda+\Delta\lambda$ originates. Since the Kα-radiation is 5/6 of the total K-radiation[18] we have for the energy of fluorescent Kα-radiation

$$E_{K\alpha}=\sum\frac{5}{6}\phi_n\frac{\delta'\omega}{4\pi}\frac{\mu_n I_n t R}{4\pi}\int_{k\epsilon}ds\int_{-\infty}^{\eta d}dx\int_0^{2\pi}d\theta\int_0^{\infty}d\tau\frac{re^{-\mu_n\sqrt{r^2+x^2}}}{r^2+x^2}e^{-\mu_{k\epsilon}(\eta d-x)} \quad (2)$$

The summation is over all wave-length ranges $\Delta\lambda$ for λ less than the wave-length of the K-absorption limit of the target. $d\tau=ds\,dx$ and $d\tau'=t\,r\,dr\,d\theta$. ηd is the depth of $d\tau$ below the surface. $\epsilon(\eta d-x)$ is the path of secondary x-rays from $d\tau'$ to the surface. s is the slit-width of the narrower slit of the collimator. h is the height of section of the focal spot of the target. By a change of variable $u=\mu\sqrt{r^2+x^2}$ this reduces to

$$E_{K\alpha}=\frac{5}{6}\frac{\delta'\omega}{4\pi}\frac{thsR}{2}\sum\phi_n\mu_n I_n\int_{-\infty}^{\eta d}-Ei(\mu x)e^{-\mu_{k\epsilon}(\eta d-x)}\,dx \quad (3)$$

Tables for the Ei function are given by Glaisher.[19] We wish to compare $E_{K\alpha}$ with the energy of the general radiation entering the ionization chamber at the same time. If we have so chosen $\Delta\lambda$ that it is equal to the complete range of wave-lengths entering the ionization chamber when it is set on the peak of the Kα line we may designate the value of I for this band I_G. The energy from an element $d\tau$ will then be $I_G d\tau$. The energy reaching the ionization chamber is given by

$$E_G=\int RI_G\frac{\delta'\omega}{4\pi}\frac{\delta\theta}{\Delta\theta}e^{-\mu'\epsilon\eta d'}d\tau \quad (4)$$

where $\delta\theta$ is the angle subtended at $d\tau$ by the slits of the collimator, $\Delta\theta$ is the maximum value of $\delta\theta$, $\epsilon\eta d'$ is the mean path of x-rays before emergence from the target, and $\delta\theta$ and $\Delta\theta$ may be expressed in terms

[19] J. W. L. Glaisher, Phil. Trans. 109, 367–387 (1870).

of the dimensions of the collimator and its distance from the target. The ratio $E_{K\alpha}/E_G$ has been calculated for copper and silver from the above expressions.

Assuming similar ideal general radiation curves for silver at $V=36{,}400$ volts and copper at $V=15{,}400$ volts in each case with the "cut off" point as prescribed by the condition $h\nu_{max}=Ve$ and the peak at the position $\nu=\nu_{max}/1.5$ we have the following for the two ratios

$$\frac{E_{K\alpha}}{E_G}=\frac{\text{Expected indirect K-radiation}}{\text{General radiation entering ionization chamber with it}}.$$

For copper $E_{K\alpha}/E_G=5.03/.54=9.3$. Unnewehr finds this ratio 11.2 so that we have accounted for about 83 percent of the Kα-radiation. For silver $E_{K\alpha}/E_G=12.6/4.8=2.62$. Unnewehr finds this ratio to be 2.7 so that in the case of silver we have accounted by this method for 97 percent of the Kα-radiation.

The discrepancy between the results for the two metals suggests that direct impact characteristic radiation may play a more important role in the case of copper than it does in the case of silver.

Estimate of Direct Impact K-Characteristic Radiation from the Target

A relative measure of the direct impact K-radiation is given by the probability that an electron of given initial velocity will approach close enough to a K-electron, before its energy has been reduced below the K-quantum, to lift it entirely out of the atom. This is the condition for direct K-characteristic radiation. To satisfy this condition the path of the electron must lie within a distance p of the K-electron where p is given by the expression[20]

$$h\nu_k=\frac{E}{1+p^2E^2/e^4} \tag{5}$$

where $h\nu_k$ is the energy necessary to lift out the K-electron, E is the energy of the impacting electron, and e is the electronic charge.

[20] It may be shown that if a body of mass m and charge e moving with velocity v approaches another body of mass m and charge e at rest that the second body will acquire a velocity u given by

$$u=v/\sqrt{1+(p^2/e^4)(\tfrac{1}{4}m^2v^4)} \tag{6}$$

where p is the perpendicular distance from the line of flight of the first particle to the second. This is derived by the mechanics of two bodies acting by the inverse law of force. Squaring and multiplying each member by $\frac{1}{2}m$ and setting $\frac{1}{2}mv^2=E$ and letting the energy acquired by the second body be $\frac{1}{2}mu^2=h\nu_k$ we have Eq. (5) above. The author is indebted to Prof. Bergen Davis for Eq. (6).

For an impacting electron of a given initial energy E_0 the probability that it will lift out a K-electron is clearly the ratio of the sum of the areas of all circles of radius p about the K-electrons to the total area of the target face. The value of this ratio is

$$2\pi n\frac{e^2}{\beta}\left[\frac{2V_0-V_k}{V_k}-\log\frac{V_0^2}{V_k^2}\right] \tag{7}$$

where β is the Whiddington coefficient of penetration in the expression $V_x^2=V_0^2-\beta x$, V_0 is the energy in abvolts of the penetrating electron, V_K is the energy just sufficient to lift out a K-electron. e is the electronic charge, and n is the number of atoms per cc in the target.

Substituting appropriate values for the two cases investigated above, silver at $V_0=36{,}400$ volts gives .00028 and copper at $V_0=15{,}400$ volts gives .00108. We should expect then about four times as many quanta of direct K-radiation from copper at 15,400 volts as from silver at 36,400 volts. In terms of energy we should expect 1.4 times as much energy from the copper as from the silver. In view of this it seems obvious that the greater part of the K-radiation is not direct impact radiation as Beatty claims for how then explain that the observed ratio of Kα-radiation of copper and silver for the above voltages is 6 to 13 when from the calculation above it should be 1.4 to 1? On the other hand we now can explain the fact that our calculated value for the Kα-line of copper was too low if for metals of low atomic number the direct K-radiation forms a considerable part of the total K-radiation but for metals of high atomic number the direct radiation becomes relatively of much less importance. This may be the explanation for the failure of molybdenum and silver to show increase in radiating efficiency in the curves for total energy as found by Brainin.

Returning to Unnewehr's data and our calculated values of Kα-radiation we have the following:

TABLE III

Target	Cu	Ag
Tube voltage	15,400	36,400
Total Kα-radiation (Unnewehr)	6.0	13.0
Indirect (fluorescent) Kα-radiation	5.03	12.6
Difference = direct impact Kα-radiation	1.0	.4

The ratio $1.0/0.4=2.5$ is in good agreement with the expected value 1.4.

As suggested above we may now make use of these results to check the validity of our determination of ϕ, the fluorescent energy transformation coefficient. If we use in place of ϕ in the calculation of indirect K-radiation from the target a value of the transformation co-

efficient derived from the assumption that $u = .87$ we shall have to substitute in Table III above 10.1 and 14.6 for the energy of the fluorescent Kα-radiation of copper and silver respectively. These values are actually larger than the total Kα-radiation observed by Unnewehr and copper now shows relatively more indirect radiation than silver. This leaves no room for any appreciable amount of the direct impact radiation which seems necessary to explain Brainin's results referred to in the preceding paragraph. These facts then seem to point to the reliability of the observed values of u as given in Table II.

Conclusions

It seems established that for any given element the ratio between the number of quanta of x-rays of any wave-length absorbed to the number of quanta of secondary K-characteristic x-rays emitted is a constant. Experimental values indicate that this quantum transformation coefficient is much less than unity and increases markedly with atomic number. This increase is further indicated by the comparison of calculated with observed values of K-radiation from the target of an x-ray tube. For copper and probably other elements of low atomic number a considerable part, but probably much less than fifty percent, of the K-radiation originates from direct impact of the cathode electrons. For silver on the other hand, and probably other elements of high atomic number, a very small part of the total K-radiation has such an origin.

I wish to express my appreciation for the interest and help of Professor Bergen Davis who suggested this research and under whose direction it was performed. Grateful acknowledgement should also be made to the Westinghouse Laboratories at Bloomfield, N. J. for the water-cooled tungsten tube used in the research.

Phoenix Physical Laboratories,
Columbia University,
February 1, 1926.

A SPECTROGRAPHIC EXAMINATION OF THE STRIATED DISCHARGE IN MIXED GASES*

By David A. Keys and M. S. Home

Abstract

The present paper contains the results of a spectroscopic examination of the striated discharge in (1) a mixture of nitrogen and hydrogen, (2) a mixture of helium and hydrogen. Spectrograms were taken of the light emitted by the negative glow and by the striations respectively. The electronic energies in the different regions of the discharge are interpreted from these spectra in much the same manner as that first suggested by Seeliger and now used by astrophysicists to determine the extent of ionization in different stars and in various levels of the sun's atmosphere from the spectra of their regions. In the nitrogen mixture the Balmer lines and the nitrogen bands 4708, 4278 and 4236 were found to appear in the negative glow but to be absent from the striations. Interpreting this result in terms of electronic energies (or equivalent quanta, if radiation) there are relatively few electrons possessing energy equivalent to 15.5 volts in the striations though the potential applied to the discharge tube was about 1100 volts. In the mixture of helium and hydrogen, the Balmer lines are strong in the striations but relatively weak in the negative glow. The line spectrum of helium was strong in the negative glow but weak or absent in the striations. The mercury arc lines were equally strong in both parts of the discharge. In terms of electronic energies, these results mean that there are relatively few electrons possessing energy equivalent to 25.3 volts in a striation but plenty possessing energies of 10.4 and 15.5 volts. An explanation is suggested of the change in intensity of certain lines in mixtures of different gases.

THE following experiments are a continuation of a former paper,[1] in which the spectra from the different regions of a striated discharge are examined with a view to determining (I) the relative concentration of the different atoms and molecules in the various excited states and (II) the distribution of potentials or electronic energy in the same regions. The distribution of potential and the electric field in different parts of a striated discharge have been measured by many investigators. The various methods which have been used may be classified under the following four groups: (A) the exploring electrode,[2] (B) the cathode ray beam,[3] (C) the Stark effect,[4] (D) the hot and cold sounding probe

* Read in abstract, Kansas City Meeting of the American Physical Society, December, 1925.

[1] D. A. Keys, Trans. Roy. Soc. Canada 19, 143 (1925).

[2] J. J. Thomson, "Conduction of Electricity through Gases." 2nd Edition p. 528.

[3] J. J. Thomson, Phil. Mag. 18, 441 (1909); F. W. Aston, Proc. Roy. Soc. A.

[4] E. Brose, Ann. d. Physik 58, 731 (1919).

method due to Langmuir.[5] The unreliability of A and the limitations of B and C are quite evident. The presence of the probe in those experiments in which the Langmuir method has been used, has been found not to distort the field appreciably. In these cases the current density has been comparatively large. But in discharges of small current densities such as are used in the present paper any obstruction in the path of the discharge is more liable to alter conditions. Moreover, under the conditions of the experiments to be described, the discontinuities in the current potential curves obtained by the Langmuir method would be very difficult to designate with accuracy. The method adopted in this paper was therefore similar to that used by Seeliger,[6] who observed the variation in intensity of certain spectral lines in different regions of a glow discharge. The light emitted by different regions of the discharge was photographed with a spectrograph and from the nature of the spectra the potentials or electronic energy necessary to produce the lines determined.* The gas is thus made to reveal its own condition and the potentials are determined in much the same manner as that used by astrophysicists[7] to determine the extent of ionization among the different atoms in the various stars and in the different depths of the stellar atmosphere of the same star, by examining the light which they emit or absorb. The method is limited by our knowledge of excitation and ionization potentials but some information may be obtained when these potentials are known. One of us has already pointed out some differences in the spectra from different parts of a single striation and the negative glow in the case of hydrogen.[1] The present paper contains the result obtained from the examination of (i) a mixture of nitrogen and hydrogen and (ii) a mixture of helium and hydrogen.

Apparatus

The apparatus used was similar to that described in an earlier paper,[1] consisting of a glass tube about 95 cm long and 5.5 cm in diameter, fitted with parallel plane aluminium electrodes. The potential difference between the electrodes was about 1100 volts and the current about 10 milli-amps. supplied by an Evershed and Vignolles direct current generator. The spectrograms were taken with a Hilger constant de-

[5] I. Langmuir, J. Frankl. Inst. **196,** 751 (1923).

[6] R. Seeliger, Ann. d. Physik **67,** 352 (1922).

* It has been suggested to the authors that the Langmuir probe method might have been used to measure the velocity distribution and thus directly test the relation suggested. We hope to try this later.

[7] Saha, Proc. Roy. Soc. **A99,** 136 (1924).

viation glass spectrograph. The tube was exhausted by a Hyvac oil pump and a charcoal tube cooled with liquid air. The gases were dried with phosphorus pentoxide and the discharge tube was washed out thoroughly several times with the gases before a photograph was taken, the discharge passing through each rinsing in order to remove as much as possible of the "residual" gases from the electrodes. No attempt was made to bake the tube or the electrodes.

Observations

Nitrogen and hydrogen. The nitrogen was prepared by heating a solution of potassium nitrite and ammonium chloride, the gas being purified by passing it over heated copper turnings to remove any trace of oxygen present and over phosphorus pentoxide to remove the water vapor. Some observations were first made on the relation between the current and the applied potential. It was found that at a certain potential the current rose rapidly without any change in potential, the pressure of the gas being about 0.01 cm of mercury. On

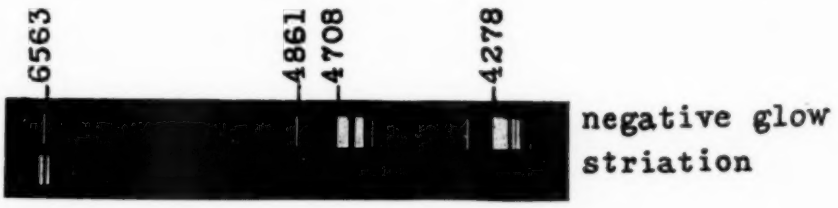


Fig. 1. Spectrogram of the striated discharge in a mixture of nitrogen and hydrogen.

reducing the potential the current did not fall to its former value, confirming Olsen and Young's observation,[8] who attribute this fact to the charging up of the walls of the tube. The potential was then kept constant at about 1100 volts and spectrograms were taken of the light emitted by the negative glow and by a striation. The results are shown in Fig. 1. It will be seen that the lines Hα and Hβ come out strongly in the negative glow but are absent in the striation. To produce the Balmer lines from molecular hydrogen requires 15.5 volts and to produce the negative bands in nitrogen requires 17.75 volts.[9] *It therefore appears that there are no electrons present in the striation possessing energy equal to 15.5 volts, though the potential between the ends of the tube is 1100 volts.* If we assume a Maxwellian distribution for the energy of electrons, the results show that the center of this

[8] A. R. Olsen and T. F. Young, Phys. Rev. **25**, 58 (1925).
[9] E. E. Witmer, Phys. Rev. **26**, 780 (1925).

distribution corresponds to an energy less than 15.5 volts in the striation.

Helium and hydrogen. Helium with a small trace of hydrogen was now used in the tube. Some interesting changes in the nature of the discharge were noticed during this washing. When the striations were first formed they were not equally spaced, the distance between the striae near the anode being only about one-half that between those near the cathode. A stria would appear to vanish in the middle of the positive column without any visible effect on its neighbors. The phenomenon lasted about a minute and was not observed in any subsequent work. This effect is attributed to nitrogen liberated by the electrodes. On commencing the discharge the striae were formed at once but were not clearly defined. After about ten minutes they became quite sharp but in an hour they commenced to degenerate into

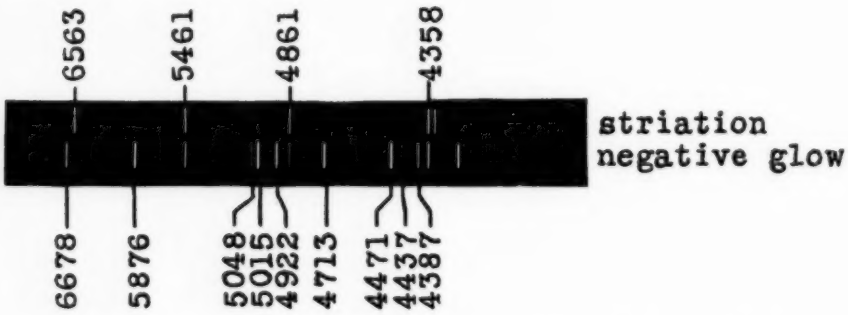


Fig. 2. Spectrogram of the striated discharge in a mixture of helium and hydrogen.

the continuous positive column and after two hours the column was continuous except for two striations near the cathode end. The current was then raised from 10 to 12 milli-amps. and in a few minutes the striae returned to their former sharpness. This was repeated several times during each washing. No visible change in pressure could be detected with the McLeod gauge during this degenerating process. All traces of nitrogen were finally removed and after leaving the tube connected for three hours with the charcoal tube cooled with liquid air, the discharge settled down to a steady state, a trace of mercury vapor and hydrogen being the only impurities present. A typical spectrum of the negative glow and of a striation is shown in Fig. 2. Table I gives some of the principal lines and their relative intensities measured in these photographs. The notation is that used by Fowler.[10]

[10] A. Fowler, "Report on Series in Line Spectra."

The table shows that the line spectrum of helium is strong in the negative glow but it is practically absent in the striation, the only series which show any tendency to persist being the $1S-mP$ and $1\pi-m\delta$.

From these sepectrograms we see that the helium lines are strong in the negative glow and very weak or absent in the striation. The hydrogen Balmer lines however are strong in the striation and weaker in the negative glow. This is just the reverse of what is the case when hydrogen alone is used.[1] The mercury lines 5461, 4358 and 4047 are

TABLE I

Lines in the spectra of the negative glow and of the striations. Helium and hydrogen mixture.

Series type	Wave-length	Negative glow	Striation
1*S*–2*P*	5015	Strong	Fairly strong
1*S*–3*P*	3965	Weak	Absent
1*P*–2*D*	6678	Strong	Very weak
1*P*–3*D*	4922	Strong	Very weak
1*P*–4*D*	4387	Strong	Very weak
1*P*–5*D*	4144	Weak	Very weak
1*P*–3*S*	5048	Strong	Absent
1*P*–4*S*	4437	Strong	Absent
1π–2δ	5876	Strong	Weak
1π–3δ	4471	Strong	Weak
1π–4δ	4026	Strong	Absent
1π–3σ	4713	Strong	Very weak
1π–4σ	4120	Weak	Absent
Hα	6563	Very weak	Strong
Hβ	4861	Fairly strong	Strong
Hg	5461	Strong	Strong
	4358	Strong	Strong
	4047	Strong	Strong

equally strong in both parts of the discharge. Interpreting these results in terms of electronic energies, *we see that relatively few electrons have energy equivalent to 25.3 volts in the striation but that a large number have energy equivalent to 10.4 volts (to produce the mercury lines) and 15.5 volts to produce the Balmer lines.*

In contrast to the behavior of hydrogen in nitrogen, the Balmer lines Hα and Hβ in the mixture of hydrogen and helium are much fainter in the negative glow than in the striation. Furthermore, the two lines in the latter case show a curious reversal of intensity in the negative glow. Hα is very faint while Hβ is much stronger though the normal intensity of Hα is greater than that of Hβ. It appears that the presence of helium in some way prevents the excitation of these two Balmer lines in the negative glow and enhances them in the stria-

tions. Merton and Pilley[11] have shown that the presence of helium at high pressures increased the intensity of the N^+ lines in the positive column and McLennan and Shrum[12] found that the presence of helium or neon brought out the famous green line 5577 in oxygen. Now we have shown that the Balmer lines are affected in the same manner, and the same explanation may be applied to their experiments as to ours, namely that the inert gases cause a redistribution of the electronic energy so that the maximum energy occurs in a region which will excite these lines in all three cases just cited. Compton[13] has given an explanation of Merton and Pilley's results as being due to optical excitation by collisions of the second kind. According to the theory of Klein and Rosseland, the probability of such excitation taking place decreases as the difference between the energy of the excited atom and that required to excite the second atom increases. The difference between the excitation potential of $H\alpha$ and $H\beta$ is very small, and, though the probability of $H\beta$ being optically excited by the excited or ionized helium in the negative glow is greater than that of $H\alpha$, the difference in this probability seems hardly sufficient to account for the result that $H\beta$ is so much stronger than $H\alpha$. Hughes and Klein[14] have shown that the fraction of the collisions of electrons with atoms and molecules which result in *ionization* increases to a maximum and then decreases as the energy of the electrons increases. On the supposition that the $H\alpha$ and $H\beta$ lines are excited directly for the most part by electrons, this reversal of intensity of $H\alpha$ and $H\beta$ in the negative glow would mean that the Maxwellian distribution of energy among the electrons in the negative glow has a maximum which has a higher energy value that that required to excite the $H\alpha$ line. In a discharge tube using a hot cathode and a mixture of mercury vapor and hydrogen, Turner and Compton[15] have shown that the arc spectrum of mercury is emitted both from the negative glow and from a striation, and Compton, Turner and McCurdy[16] found no trace of the hydrogen lines in the striations in a similar experiment, while the Hg bands were found in the striations. This is a result similar to the behavior of hydrogen as found in our experiments. Work is being continued using still larger discharge tubes and different gasseous mixtures to see how the

[11] T. R. Merton and J. C. Pilley, Proc. Roy. Soc. **A107**, 411 (1925).
[12] J. C. McLennan and J. M. Shrum, Proc. Roy. Soc. **A 108**, 501 (1925).
[13] K. T. Compton, Phil. Mag. **50**, 512 (1925).
[14] A. L. Hughes and E. Klein, Phys. Rev. **23**, 450 (1925).
[15] L. A. Turner and K. T. Compton, Phys. Rev. **25**, 606 (1925).
[16] K. T. Compton, L. A. Turner and W. H. McCurdy, Phys. Rev. **24**, 597 (1924).

distribution is affected by the diameter of the tube, the different gases present and their relative concentrations.

Conclusion

1. Spectrograms have been taken of the negative glow and of a striation in mixtures of (i) nitrogen and hydrogen (ii) helium and hydrogen.

2. In the case of the nitrogen mixture, the Balmer lines Hα and Hβ and the nitrogen bands 4708 and 4278 appear in the negative glow, but are absent from the striation.

3. In a mixture of helium and a trace of hydrogen the helium line spectrum is strong in the negative glow but weak or absent in the striations. The hydrogen lines are strong in the striations but relatively weak in the negative glow. The mercury lines are strong in both parts of the discharge. Hα is much weaker than Hβ in the negative glow.

4. A method of interpreting the electronic energies in different parts of the discharge from the spectra emitted has been followed. On this hypothesis there are relatively few electrons possessing energy equivalent to 15.5 volts in the striations in the nitrogen mixture. Also in the case of the helium mixture, a relatively small number of electrons have energy equivalent to 25.3 volts, but there are plenty with energies equivalent to 10.4 and 15.5 volts in a striation.

5. An explanation of this change in the distribution of the intensity of certain lines in mixtures of gases is suggested on the supposition of a change in the position of the peak of the Maxwellian distribution of energy among the electrons.

The MacDonald Physics Building,
McGill University,
February 15, 1926.

THE FORMATION OF NEGATIVE IONS IN MERCURY VAPOR

By Walter M. Nielsen

Abstract

The method used is similar to that of Mohler. Electrons, projected along the axis of a tube between two plates were prevented from scattering by a magnetic field of 350 gauss parallel to the axis of the tube. Negative ions formed by the attachment of an electron to an atom or to a molecule were removed by suitable potentials applied to the side plates. The remainder of the current reached a circular plate at the end of the tube. With a small field between the side plates, the negative ion current was just barely observeable (1×10^{-10} amperes). With higher fields the ion current increased enormously, approaching saturation when the potential difference between the side plates was increased to between 3 and 4 volts. In this report the ion currents were of the order of 9×10^{-9} amperes. The total current was of the order of 1×10^{-7} amperes.

The ratio between the negative ion and total current decreases with increase in the driving potential for low voltages, but increases at 2.7, 4.7, 5.5, and 8.8 volts. The decrease at low potentials is similar to the results of Mohler in other gases and vapors. The cause of the break at 2.7 volts is not known. The breaks at 4.7, 5.5, and 8.8 volts are believed to be associated with the electronegative properties of the mercury atom having an electron in a metastable orbit. The total current rises rapidly with increase in the driving potential and decreases at 4.9 and 6.7 volts.

Introduction

F. L. MOHLER[1] has recently published a report on the production of negative and positive ions in a number of vapors and gases including mercury vapor. He projected a beam of electrons along the axis of a cylinder in an approximately equipotential region with a magnetic field of 100 gauss parallel to it. He then applied a positive or negative potential of one volt to the cylinder, measuring in each case the negative or positive current to it. He concluded that under the conditions of his experiment, the number of negative ions formed at low pressure was small compared to the number of positive ions formed above the ionization potential. No negative ions were observed in mercury vapor for impinging electrons having speeds less than 10.4 volts.

The present investigation is concerned with a somewhat similar attempt to study the formation of negative ions in mercury vapor. Under conditions which are believed to approximate those in the above work, similar results were obtained, but under different conditions,

[1] F. L. Mohler, Phys. Rev. 26, 614–624 (1925).

results were obtained which are regarded as evidence for the existence of negative ions of mercury vapor.

Experimental Apparatus

The apparatus and electrical circuit are shown in Fig. 1. Electrons from a filament F were projected along the axis of a Pyrex tube by means of a potential V_F between the filament and a diaphram C. Two plates, P_1 and P_2, were placed in a skew position as shown. Electrons were prevented from reaching them by placing the tube in the core of a solenoid so that the lines of force in the region between C and a circular plate P_3 were parallel to the axis of the tube. The

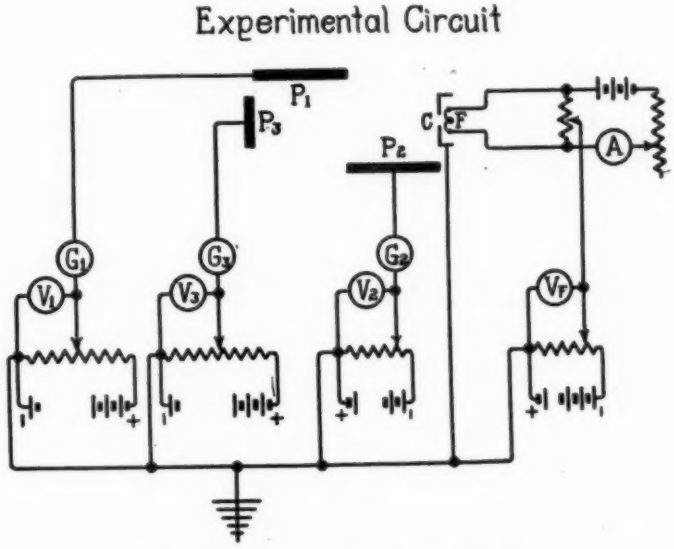


Fig. 1. Apparatus and electrical circuit.

intensity of the field was about 350 gauss. Outside the plates P_1 and P_2 and next the glass wall was a grounded gauze to eliminate extraneous surface potentials. All metal parts with the exception of the tungsten filament were of copper. The filament assembly was provided with a ground glass joint and mercury seal to facilitate replacement. The source of electrons was a tungsten spiral of one loop placed so that its elements were perpendicular to the axis of the tube.

Galvanometers and suitable sources of potential were connected to the plates P_1, P_2, and P_3. V_3 was generally a fraction of a volt higher than V_1, both being positive with respect to C. Under such conditions, electrons brought to rest as the result of inelastic collision

would be attracted downward and would not therefore have a tendency to diffuse from the center of the tube as apparently occurred in the experiments of Richardson and Chaudhuri.[2] The galvanometer G_1 measured the current i_1 due to the negative charges which were able to drift to P_1 in spite of the magnetic field. This current increased rapidly with increase in the electric field between the side plates so that it was necessary to apply to them a potential difference of between 3 and 4 volts to attain saturation. The galvanometer G_2 was intended to measure the positive ion current i_2. The galvanometer G_3 measured the negative current i_3.

The vapor pressure in the tube was about .003 mm of mercury, a pressure corresponding to the temperature of the mercury seal during the observations.

Results and Discussion

With a low filament temperature, readings were taken simultaneously of i_1, i_2, and i_3, for different values of the driving potential. In most of the present work G_2 was used to indicate the ionization potential only. Dividing the current to P_1 by that reaching P_1 and P_3, a fraction R is obtained which gives the ratio between the negative ion and total current. If, as in this report, the negative ion currents are saturation currents, this number is proportional to the number of negative ions formed per unit electron current. The results are shown by the curve of Fig. 2. In this case, V_1 was 3 volts, V_3 was 3.2 volts and V_2 was zero. The potentials are corrected for initial velocity, etc., assuming the ionization potential of mercury to be 10.4 volts. The ion current was of the order of 9×10^{-9} amperes and the total current was of the order of 1×10^{-7} amperes.

The curves shown in Fig. 2, as well as those in Fig. 3 and Fig. 4 to follow, are representative of several taken over the same range under approximately the same conditions. While the currents vary somewhat because of differences in the intensity of the magnetic field, the critical points are all reproducible with the exception of a kink on the ratio curve at 7.7 volts, which did not appear on some of the curves. It did not appear on the curve of Fig. 2. It is quite astonishing that the breaks are so definite in view of the relatively large potentials on P_1 and P_3 which would be expected to blur out the effects. The fact that changes in these potentials did not produce marked changes in the critical points was proved experimentally. A change in the poten-

[2] Richardson and Chaudhuri, Phil. Mag. 45, 337–52 (1923).

tial difference between P_1 and P_2 of 1 volt, lowered the value of V_F necessary to produce ionization by .1 volt.

That the currents observed above are in some way due to the presence of the mercury vapor was proved by removing the vapor. Carbon dioxide snow was applied to the mercury trap while the tube and connecting glassware were heated. After a few hours it was found that the negative ion current had been reduced to such an extent as not to be detectable with the galvanometer used. That such observed currents are due to electrons which have collided a number of times

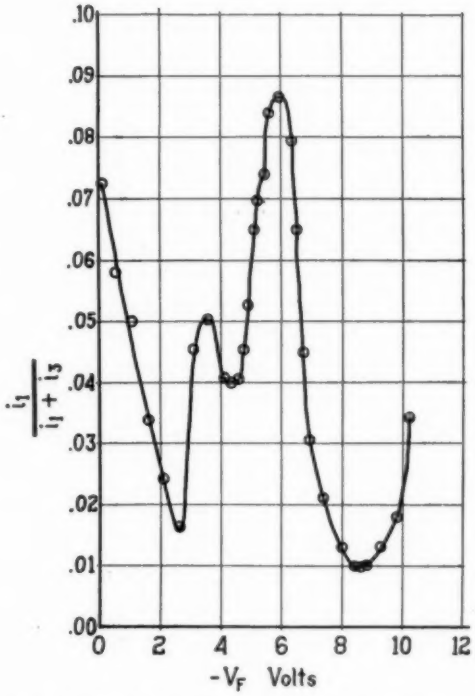


Fig. 2. Variation of the ratio of negative to total current with accelerating potential. $V_1=3.0$ volts, $V_2=0.0$ volts, and $V_3=3.2$ volts.

is quite improbable because of the low vapor pressure and because the experimental conditions, to some extent, prevented electron diffusion. One would expect that some of the electrons deflected in such a manner would have energy corresponding to V_F. To test this point, with V_1 and V_2 equal to zero, and with V_3 equal to 1.1 volts, it was found that the current to P_1 was not detectable for all values of V_F below the ionization potential. Indeed, it must be emphasized that it was necessary that V_1 be of the order of 2 or 3 volts positive in order to attract

the negative charges to P_1 and cause currents of the order of 9×10^{-9} amperes as observed above. Whether or not Mohler's failure to observe these negative charges is due to this fact, is not known. In neither case do the electric fields lend themselves to computation. With a potential of 1 volt positive on P_1, the negative ion current was barely observable, being about 1×10^{-10} amperes. The radius of curvature of a 10 volt electron traveling initially at right angles to the axis of the tube in a magnetic field of the order used is about .6 mm. It seems unlikely, therefore, that the increased potential of P_1 would increase electron scattering to the walls. Because of the above facts, it seems necessary to believe that it is possible under certain circumstances for an electron to attach itself to a mercury atom or molecule.

The decrease in the ratio curve of Fig. 2 is similar to the effect observed by Mohler[1] in other gases and vapors. To explain this, he assumed that only slowly moving electrons attach themselves to molecules to form negative ions. At potentials equal to potentials of inelastic collision he observes an increase in the negative ion current in agreement with his theory. Accepting this view, one would expect an increase in the ratio curve at 4.9 volts in mercury vapor. That no kink was observed, may be due to the fact that the resolving power of the apparatus was not sufficient to distinguish it from an effect setting in at about 4.7 volts. The increase at 2.7 volts cannot be correlated with the critical potentials of the mercury atom. Possibly it is of molecular structure, although mercury vapor is generally regarded as monatomic. The mercury atom is known to have two metastable orbits corresponding to about 4.7 and 5.5 volts. The $2p_3$ orbit has a computed energy of 4.66 volts and the $2p_1$ orbit has a computed energy of 5.43 volts. Critical potentials at 4.68 and 5.47 volts have been observed by Franck and Einsporn.[3] There is evidence that an excited atom possesses an electron affinity and hence tends to form negative ions.[4] Because of these facts, the breaks in the ratio curve at 4.7 and 5.5 volts have been interpreted as being critical potentials for the formation of negative ions of mercury vapor. The rise in the curve at 8.8 volts may be interpreted to support that view. Franck and Einsporn[3] list a number of levels which they associate with an observed critical potential of 8.8 volts. The levels $3p_1$, $3d_1$, $3d_2$, $3d_3$, and $3P$ have computed potentials ranging from 8.79 to 8.82 volts. While some of these levels are

[3] Franck and Einsporn, Zeits. f. Physik **2**, 18–29 (1920).

[4] See for example Franck and Grotian, Zeits. f. Physik **4**, 89–90 (1921); Compton, K. T., Lilly, E. G., and Olmstead, Phys. Rev. **16**, 282–289 (1920); Davis, A. C., Proc. Roy. Soc. **100A**, 599–620 (1922).

metastable, those which are not, revert to levels of lower energy by the emission of mono-chromatic radiation. In particular, some of them will return to the $2p_1$ and $2p_3$ orbits, making the atom susceptible to the formation of a negative ion. An increase in the ratio of negative ion to total current would therefore be expected from this view-point when the impinging electron is able at collision to remove the valence electron to the $3p_1$, $3d_1$, $3d_2$, $3d_3$, and $3P$ levels. Since an additional electron is necessary for the formation of a negative ion, it seems quite possible that the impinging electron having lost all of its energy, would remain attached to the atom or molecule with which it collided.

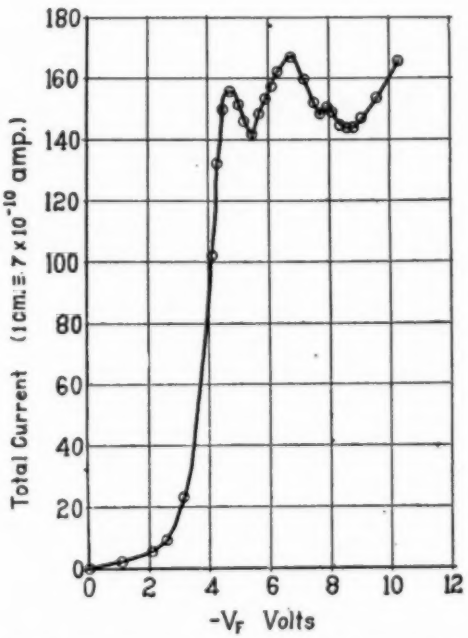


Fig. 3. Variation of total current with accelerating potential. V_1, V_2, and V_3, same as in Fig. 2.

Fig. 3 gives the variation of the total current with the driving potential. The two breaks in the curve at 4.9 and 6.7 volts correspond to the two prominent resonance potentials of the mercury atom. That the negative ions were instrumental in decreasing the total current is shown by the curves of Fig. 4, which show the variation in the total current for different positive potentials on P_3. In A, V_3 was 0 volts, in B, V_3 was 1.1 volts, and in C, V_3 was 3.2 volts. The fact that curve A shows no breaks may be attributed to the fact that possibly under

such conditions very few of the electrons have energies corresponding to V_F because of space charge. With higher values of V_3, such as with B and C, the total current rises more rapidly but then seems to drop off in the region in which large numbers of slowly moving ions are formed. If now a potential is applied to P_1, such as in curve D of Fig. 4 and in the curve of Fig. 3, the total current is enormously increased, particularly in the region of 5 and 6 volts. In the case of curve D, Fig. 4, practically none of the negative ions reached P_1, although apparently some of them have been removed to a more ineffective part of the tube.

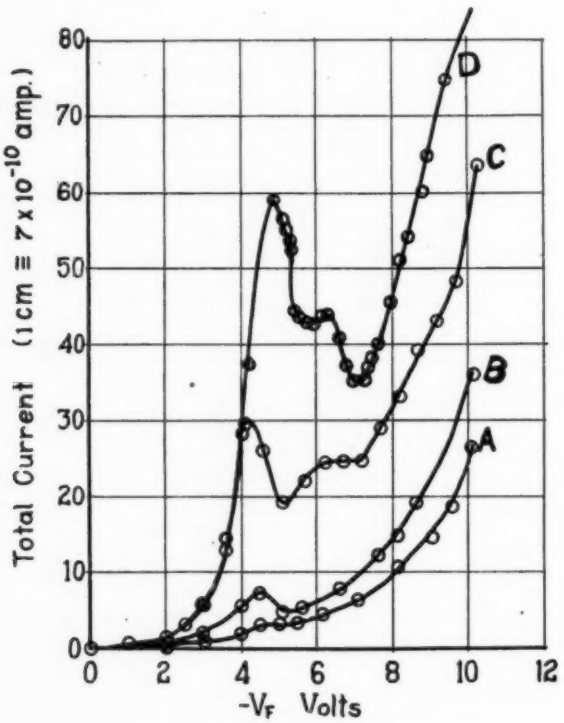


Fig. 4. Variation of total current with accelerating potential. $V_1=0.0$ volts, $V_2=0.0$ volts, in A, B, and C. In A, $V_3=0.0$ volts, in B, $V_3=1.1$ volts, and in C, $V_3=3.2$ volts. In D, $V_1=1.1$ volts, $V_2=0.0$ volts, and $V_3=3.2$ volts.

The drop in the curve at 5.5 volts may be associated with the increase in the ratio curve of Fig. 2 at about this potential. In the case of Fig. 3, however, the abrupt increase in the total current at this potential as well as at 8.8 volts are difficult to reconcile with the present interpretation of the data.

It is hoped that work now in progress with a tube of greater resolving power will furnish additional information on the current voltage characteristics of the electron beam and on the nature of the break at 2.7 volts.

The writer acknowledges with pleasure the encouragement and advice of Professor John T. Tate.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
February 9, 1926.

PROBABILITY OF IONIZATION OF GAS MOLECULES BY ELECTRON IMPACTS. II CRITIQUE

By K. T. Compton and C. C. Van Voorhis

Abstract

Corrections to results of Hughes and Klein. Three sources of error are found and approximate corrections for them determined. They are (1) an effect of the electric field on the effective area of holes in the grid through which the primary electrons pass, which introduces corrections varying from −18 percent at the lowest voltages to +14 percent at 300 volts; (2)presence of slow secondary electrons and lack of uniform velocity of electrons in the primary electron stream, which necessitate additive corrections ranging from 30 to 50 percent; (3) warming of the gas by the filament, necessitating an additive correction of 12 percent. *Correction to our previous results.* Owing to lack of uniformity of velocities of electrons in the primary electron stream, we must add corrections of 24 percent at 45 volts, 11 percent at 100 volts and 9 percent beyond 125 volts. With these corrections the results from these two sets of experiments are in fair agreement. Curves show the final values for the probability that an ionizing collision will be made in a cm path in the gas at 0.01 mm pressure and 25°C by an electron of any speed up to 400 volts in He, Ne, A, H_2, N_2, Hg, HCl, and also for the probabilities of ionization at an impact in these gases.

SEVERAL attempts have been made to measure directly the average ionization per centimeter path by an electron moving with known speed through a gas at definite pressure, leading to calculations of the probability of ionization at a collision as a function of the speed of the electron and the nature of the gas. Of the three recent investigations of this subject, two[1] are in qualitative agreement with each other and with earlier work,[2] while the third[3] presents unique results. The present paper is devoted to an investigation of sources of error inherent in the methods which have been used and to the correction of previous results.

In our earlier paper we pointed out that our values for probability of ionization could hardly be too large, owing to the rather direct method of making the measurements. Since the values reported by Hughes and Klein were much smaller than ours (25 to 40 percent), we constructed and tested an apparatus built to duplicate as nearly as possible the essential features of their apparatus and found inherent

[1] Hughes and Klein, Phys. Rev. **23**, 450 (1924); Compton and Van Voorhis, Phys. Rev. **26**, 436 (1925).

[2] Lenard, Ann. der Physik. **12**, 474 (1903); **15**, 484 (1904); Kossel, Ann. der Physik **37**, 393 (1912); Mayer, Ann. der Physik **45**, 1 (1914).

[3] Jesse, Phys. Rev. **26**, 208 (1925).

in their method two considerable sources of error which, together with a third error mentioned in our preceding paper, explain the low values obtained by them. The filament F, grid G and plate P were similar to the electrodes used by Hughes and Klein, but the collector C was added for reasons which will be apparent. In particular the holes in the grid were made of the same size as those in Hughes and Klein's apparatus.

Hughes and Klein measured the ionization by the positive ion current to P when a field V_1 greater than the accelerating field V_a was applied to prevent the primary electrons from the filament from reaching it. In order to measure the primary current through the grid, they reversed the field V_1 into the direction V_2 and measured the electron current to P. This current increased slowly linearly with V_2

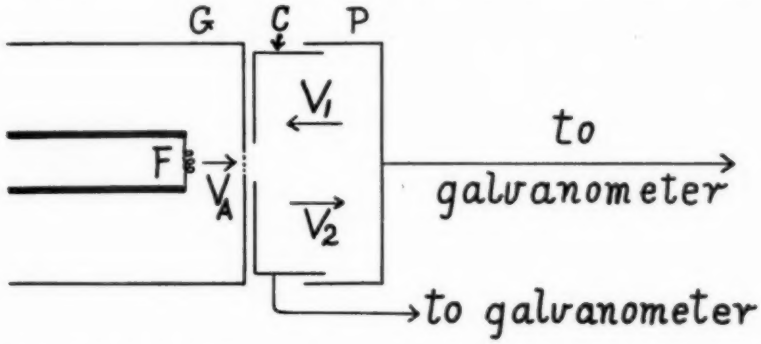


Fig. 1. Apparatus for measuring probability of ionization by the method of Hughes and Klein. The collector C was added to permit measurement of primary electron current.

for values of V_2 greater than V_a, and they assumed that by extrapolating this back to the field V_1 they would find the primary current through the grid for the field V_1.

Now this variation of electron current to P with V_2 is due in part to the action of the field on the *effective open area of the holes in the grid.* In other words, a large field V_2 will pull through the holes some electrons which, with smaller fields, would have struck the grid near these holes. A consideration of the geometry of the electric field near such holes suggested that the relation between current and field V_2 should be nearly linear *only for large values of* V_2 and that linear extrapolation through $V_2=0$ to the oppositely directed V_1 is unjustifiable.

To measure the error introduced by Hughes and Klein's extrapolation method, we measured directly the primary current through the grid, with the field V_1 just so large that no electrons reached P, by

measuring the current to C which was kept at the same potential as the grid G. Then with the same fixed value of accelerating field V_a, the current to P was measured for various values of field V_2, as was done by Hughes and Klein. The results are shown in Fig. 2 in which A is the direct measurement whereas B is the value which would have been taken by the extrapolation method of Hughes and Klein. It should be noted that the direct measurement is too small, because some of the primary electrons return again through the hole in C and are not detected. The hole in C had an area of about 10 percent of the whole area of C and we think that 15 percent is probably an upper

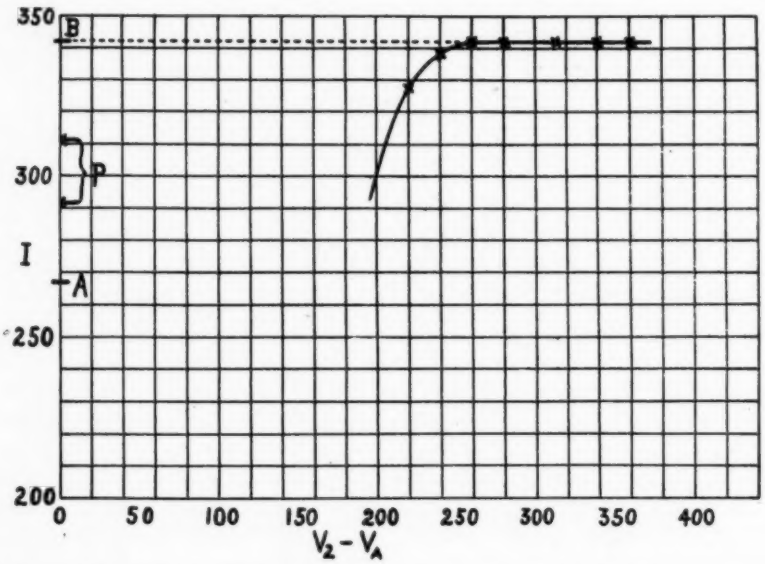


Fig. 2. Effect of retarding or accelerating field on the number of electrons passing through the holes in G. A is the actual primary electron current with sufficient retarding field to prevent electrons from reaching plate. P is this current corrected for loss through the hole in C. B is the current as estimated by Hughes and Klein.

limit to the fraction of the primary electrons which thus escape. Thus the true primary current effective in the ionization experiments should be about that indicated by P instead of B. Similar tests were made at various accelerating fields V_a. The curve I of Fig. 3 indicates the approximate corrections which should be made to Hughes and Klein's results at various voltages to take account of this source of error.

Considerably more serious is an error due to the fact that the primary electron stream, thus measured, contains a large proportion of slow secondary electrons from the grid, which contribute little or nothing to the ionization. The existence of large numbers of slow secondaries

in this type of apparatus was demonstrated recently by Lehman and Osgood.[4] We made tests of the distribution of velocities of the electrons passing through the grid, by measuring the current to P for various retarding fields V_1 between 0 and V_a, and repeated this at various values of the accelerating field V_a. Without showing these curves, the following results may be stated as clearly indicated: (1) There is an ineffective group of secondaries amounting to about 15 percent at 50 volts, 22 percent at 98.5 volts, 33 percent at 151 volts, 40 percent at 202 volts and 42 percent at 290 volts. (2) The remaining effective group of electrons at each accelerating voltage is fairly homogeneous,

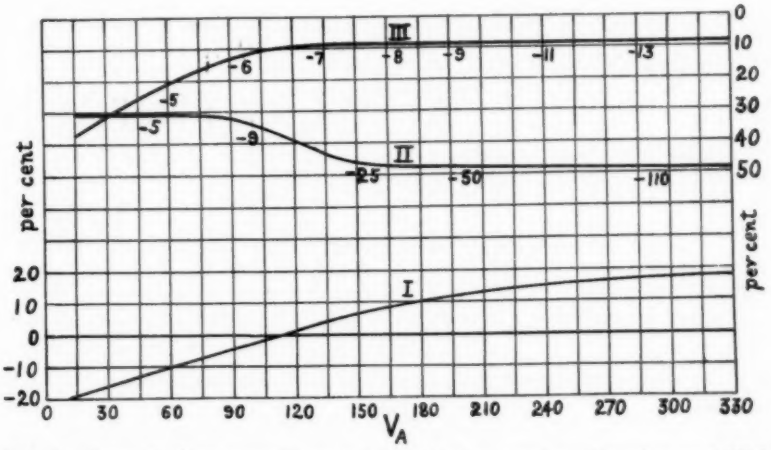


Fig. 3. Curve I gives corerctions to be applied to results of Hughes and Klein on account of the effect of the field on the number of electrons passing through the grid. Curve II gives the corrections to results of Hughes and Klein due to inhomogeneity of the primary electron beam. Curve III gives the correction due to the same cause applicable to the experiments of Compton and Van Voohris.

in that most of them have nearly the energy corresponding to the applied field, but there is always an appreciable group with variously diminished energies.

It is clearly incorrect, therefore to assume, as did Hughes and Klein, that every electron found in the primary beam has energy corresponding to the accelerating field. It is necessary first to subtract the ineffective group of slow secondaries and then to make a step by step correction to take account of the velocity distribution among the remaining electrons which are able to ionize. These corrections to Hughes and Klein's results may be made to at least the right order of magnitude by use of curve II, Fig. 3. The ordinate at any voltage V_a

[4] Lehman and Osgood, Proc. Camb. Phil. Soc. **22**, 731 (1925).

is the percentage of Hughes and Klein's value of probability of ionization at voltage $V_a - \delta$ (where δ is the number marked on the curve) which should be added to their value for voltage V_a in order to give a value of this probability at voltage V_a, which is thus corrected for the neglect of the inhomogeneity in the velocities of electrons in the primary beam.

For example, at $V_a = 150$ volts, the correction to Hughes and Klein's probability of ionization, from this cause, is the addition to their value for 150 volts of 46 percent of their value for $150 - 25$ or 125 volts.

Finally, as we suggested in our previous paper, Hughes and Klein neglected the decrease in gas density in the region of ionization caused

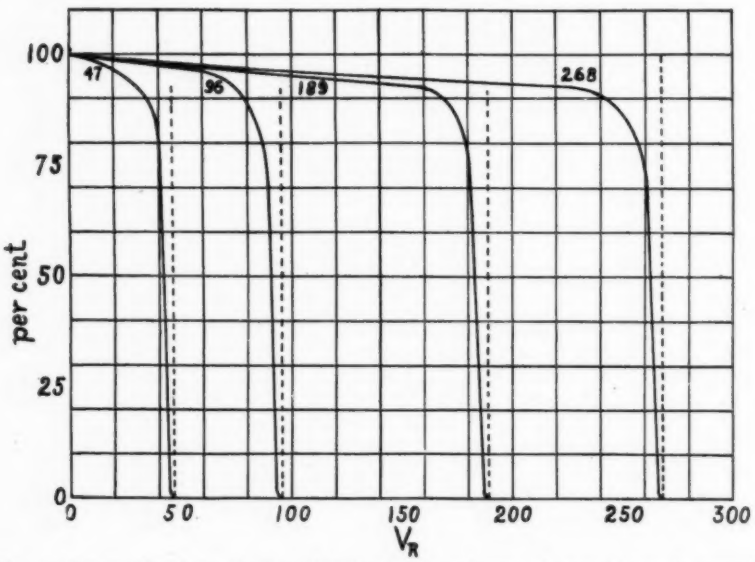


Fig. 4. Curve showing velocity distribution in primary electron beam in experiments of Compton and Van Voorhis.

by the warming of the gas by heat from the filament. In our experiments this amounted to a rise of about 25°C above the temperature of the room. The electrode arrangement of Hughes and Kein would indicate rather greater warming than in our apparatus. As a guess, which is probably fairly accurate, we may take the gas temperature in their experiments to be 60°C, which necessitates an increase of about 12 percent in all their values of probability of ionization.

Thus, to all probabilities reported by Hughes and Klein, should be added three corrections whose values are given approximately as follows: (1) a correction for variation in effective size of grid holes given by Fig. 3, curve I; (2) a correction for secondary electrons and velocity

distribution of primary electrons given by curve II; (3) a correction of 12 percent for the warming of the gas by the filament.

Turning now to the values which we previously reported, we may note that the first and third corrections described in the preceding

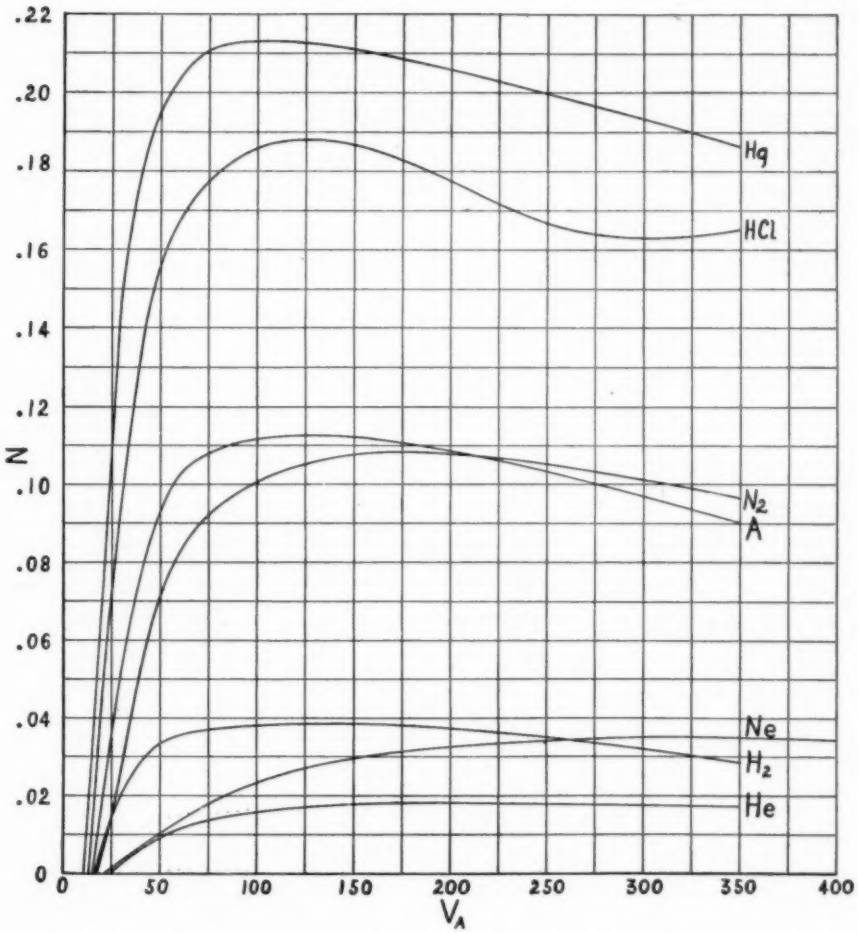


Fig. 5. Curves showing the number N of ionizing collisions made per cm path through gas at 0.01 mm pressure at 25°C.

paragraph do not need to be considered, since they were eliminated or allowed for in our original experiments. We did not, however, sufficiently consider the second source of error,—that due to velocity distribution in the primary electron stream. We have, therefore, measured the velocity distributions for various accelerating fields V_a in our original apparatus, with results shown in Fig. 4. The collecting

field V_r held back all secondary electrons, so that we were not subjected to error from the phenomenon described by Lehman and Osgood The lack of homogeneity in our electron stream, however, leads to the necessity of a correction to our previous results of an amount shown in Fig. 3, curve III, which was derived from velocity distribution curves like those in Fig. 4, by the same method employed in obtaining curve II

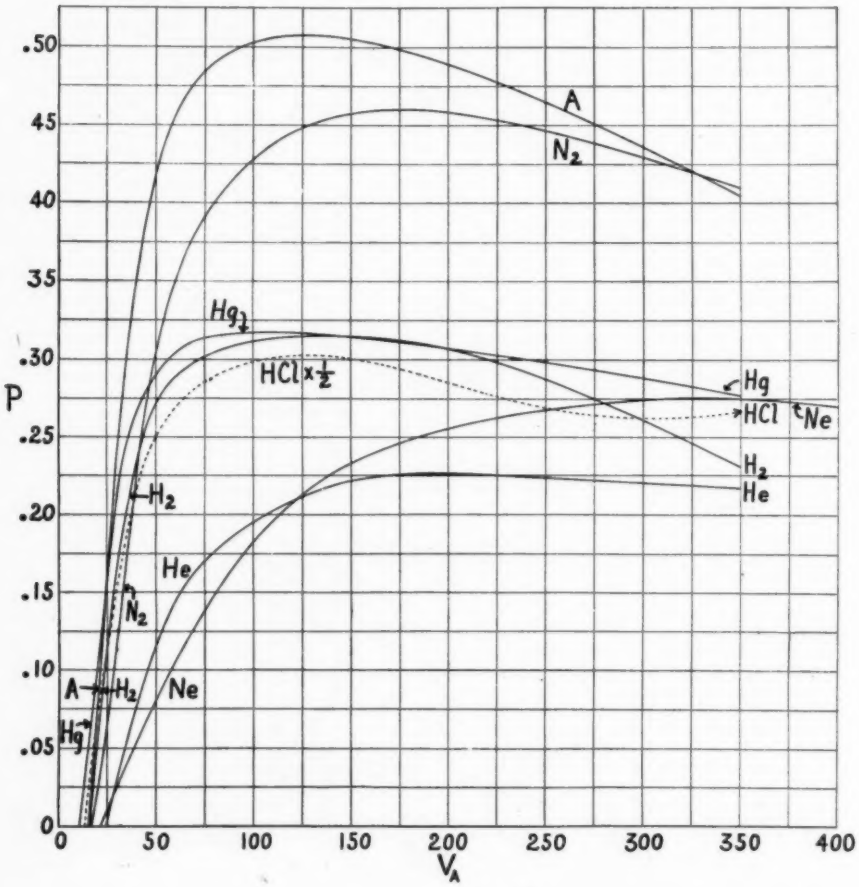


Fig. 6. Curves showing probability of ionization at a collision as a function of the speed of the impacting electron in volts.

for Hughes and Klein's results. Thus, for instance, we must add to our previous value for the ionization by 150 volt electrons, 8.5 percent of our value at 142 volts.

That the values finally arrived at in this way are fairly accurate is indicated by a comparison of our corrected results with the corrected

results of Hughes and Klein, as shown in Table I. In view of the magnitude and approximate character of the corrections in the latter case, we believe the agreement is satisfactory.

TABLE I

Comparison of probabilities of ionization from corrected results of Compton and Van Voorhis and of Hughes and Klein.

Va (volts)	Helium		Neon		Argon		Hydrogen		Nitrogen	
	C&VV	H&K	C&VV	H&K	C&VV	H&K	C&VV	H&K	C&VV	H&K
50	.115	.109	.083	.080	.430	.434	.259	.262	.310	.333
100	.197	.155	.181	.183	.500	.496	.310	.286	.425	.457
200	.227	.201	.255	.256	.490	.527	.303	.291	.457	.502
300	.219	.175	.274	.244	.436	.473	.259	.230	.430	.422

In Figs. 5 and 6 we give the final corrected values calculated from our experiments. The values of electronic mean free paths used in calculating the probabilities shown in Fig. 6 are, for 1 mm gas pressure at 25°C, He(0.1259), Ne(0.0787), A(0.045), H_2(0.0817), N_2(0.0425), Hg(0.0149), HCl(0.0322) in cm.

Finally we have made some attempts to reconcile with these results the values reported by Jesse.[3] The complicated geometry of the electric fields, the existence of secondary and perhaps tertiary electron emission and the presence of the exposed insulating walls of the glass vessel have all been shown to introduce complicating effects, so that we have not succeeded in showing how his results may be brought into agreement with the others. Jesse cites evidence to show that his second "maximum" is spurious. Neglecting this, his results are in rough agreement with ours, as was shown in our earlier paper.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.
March 1, 1926.

THE IONIZATION OF OXYGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS

By T. R. Hogness and E. G. Lunn

Abstract

Using an apparatus previously described, in which ions formed by impact of electrons of definite energy are analyzed by Dempster's positive ray method, the relative numbers of O_1^+ and O_2^+ are measured at different pressures and electron energies. Over a range of pressure from $<10^{-5}$ to 10^{-2} mm of mercury in pure oxygen, and over a large range of partial pressures of oxygen in mixtures with helium and with argon, the ratio O_2^+/O_1^+ remains practically constant. Evidence is thus given that O_2^+ and O_1^+ are formed by independent primary processes and, therefore, that an impact electron of sufficient energy can either ionize the molecule and form O_2^+ or dissociate the molecule forming O_1^+. The ionization potentials were determined: $O_2 = O_2^+ + \epsilon$; 13 volts and $O_2 = O_1^+ + O + \epsilon$; 20 volts. The latter, together with the ionizing potential of atomic oxygen, gives 6.5 volts (150,000 cal. per mol) for the heat of dissociation of oxygen. Both molecular and atomic negative ions were found. The above results are correlated with band-spectra data, with the recent theory of Franck on dissociation by absorption of radiation, and with the structure of the oxygen molecule.

THE following paper discusses experiments on oxygen made with the previously described[1,2,3] method for the positive ray analysis of the products of electron impact ionization in gases.

Experimental Details

The apparatus was that previously employed, except that the slits were narrowed to permit the use of higher pressures in the ionization tube, and to increase the resolving power. The increased resolving power was necessitated by the impossibility of freeing the oxide-coated platinum filament from all traces of residual gases, and the consequent appearance of peaks due to these impurities; these peaks, though small, would, with lower resolution, merge into the oxygen peaks and vitiate the measurements of their intensity. The ions of these impurities are presumed, from their specific charges, to be: Hg^+, CaO^+, CO_2^+, $30 = ?$, $29 = ?$, N_2^+, $20 = ?$, $19 = ?$, H_2O^+, OH^+, O^+, $15 = ?$, N^+ and C^+. With the slits narrowed to 0.28 mm these peaks are sharp and well separated. The mercury peak disappears after liquid air has been on the traps for some days, while the other peaks either disappear or become negligibly small after prolonged heating of the filament. Judging from the peak intensities obtained in previous

work with very low pressures of hydrogen[2] and nitrogen,[3] the partial pressures of the above impurities were $<10^{-6}$ mm of mercury, except in those experiments in which the highest filament temperatures were employed.

The oxygen was prepared by electrolysis of aqueous barium hydroxide and was dried with phosphorus pentoxide. Before entering the ionization tube it passed through a liquid air trap.

Positive ions. As shown by the figure, the relative intensity of the ions O_1^+ and O_2^+, as measured by the ratio of the peak intensities, remains practically constant over a range of pressure from $<10^{-5}$ to 10^{-2} millimeters of mercury. Evidence is thus given that O_1^+ and

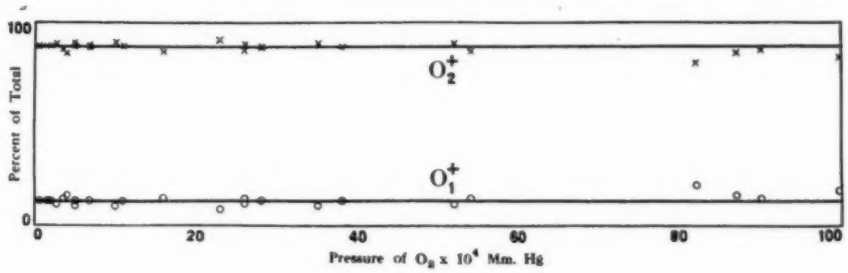


Fig. 1. Precentage of 0_1^+ and 0_2^+ as a function of pressure.

O_2^+ are formed by independent processes, and hence that an impact electron of sufficient velocity can either produce an O_2^+ ion which does not dissociate on collision with gas molecules:

$$O_2 = O_2^+ + \epsilon \,, \tag{1}$$

or it can dissociate the molecule and ionize one atom as the primary process:

$$O_2 = O_1^+ + O + \epsilon \,. \tag{2}$$

The slight increase in the percentage of O_1^+ at the higher pressures is probably due to the formation of these ions from the impurities, for, owing to a specific inhibiting effect of oxygen on the emission of electrons from an oxide-coated filament,[4] it was necessary to raise the filament to a high temperature and hence to increase the concentration of those foreign gases which, on ionization, produce O_1^+-ions.

The relative intensities of O_1^+ and O_2^+ were found to be nearly independent of other experimental conditions, such as the partial

[1] Hogness and Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924).
[2] Hogness and Lunn, Phys. Rev. **26**, 44 (1925).
[3] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).
[4] Koller, Phys. Rev. **25**, 671 (1925).

pressure of oxygen in mixtures with helium and with argon, and the speed of the positive ions in the ionization chamber.

In mixtures of oxygen with helium and with argon the percentage of O_1^+ was found to be only slightly larger than in pure oxygen, and this slight increase is probably caused by O_1^+ ions from the impurities due to the high filament temperature made necessary by the small partial pressure of the oxygen. With argon in the tube, peaks of specific charges 40 and 36 (referred to 0 = 16) appeared, thus confirming Aston's[5] evidence on the isotopy of argon.

The relative intensities of O_1^+ and O_2^+ are practically independent of the energy of the impact electron from 50 to 200 volts; above 200 and up to 600 volts, increasing this energy gradually decreases the percentage of O_1^+. Similarly, varying the speed of the positive ions in the ionization chamber by changing the field V_3 from 0 to 31 volts does not change the intensity ratio appreciably.

Ionization potentials. The ionization potentials for the formation of O_2^+ and O_1^+ were determined by comparing their disappearing potentials with that of helium in essentially the manner previously described.[2] Oxygen was mixed with helium in the reservoir until the "saturation" intensities of He^+ and O_2^+ were the same, and the disappearing potentials compared; the concentration of oxygen was then increased until the He^+ and O_1^+ "saturation" intensities were equal, and the disappearing potentials of these ions were then measured. Taking 24.5 volts as the ionization potential of helium,[6] the mean of six determinations gave 13 volts as the ionization potential for the formation of O_2^+ and 20 volts for the formation of O_1^+.

Negative ions. On reversing the magnetic field and the electrical fields V_3 and V_4, the negative ions O_2^- and O_1^- were observed. These had previously been found by J. J. Thomson.[7] The atomic ion was the more intense under all conditions studied; but the intensities of both O_1^- and O_2^- were so small as to preclude the possibility of their formation being related to the positive ion process.

Discussion

The ionization of oxygen has been studied by McHenry[8] and by Smyth.[9] McHenry used Thomson's positive-ray apparatus and hence

[5] Aston, Phil. Mag. **39**, 611 (1920).
[6] Lyman, Science **56**, 167 (1922).
[7] J. J. Thomson, Rays of Positive Electricity, p. 71.
[8] McHenry, Phil. Mag. **45**, 433 (1923).
[9] Smyth, Proc. Roy. Soc. **105 A**, 116 (1924).

experimental conditions that make difficult any comparison of his results with those above. The present results differ somewhat from those of Smyth. His published curves show a larger percentage of O_1^+ than was found above; this is perhaps due to the presence of N_1^+ and other impurities not resolved by his apparatus. The ion of apparent $m/e=8$, which Smyth observed, was probably not O^{++}. In the present work its peak appeared as a very broad one of small height—indicative of formation by some secondary process, such as the disruption of an O_2^+-ion which had fallen through the full analyzing field.[10] The above experiments show no evidence of the discontinuity in the ionization curves at 450 volts found by Smyth. His measurements gave 15.5 and 23.0 volts as the ionization potentials. We believe Smyth's values for these ionization potentials to be in error, owing, perhaps, to incorrect initial velocity corrections; but their difference ($23.0-15.5=7.5$ volts) agrees well with that (7 volts) found above.

Of the several determinations of the ionizing potentials of oxygen[11] only that of Mackay[12] shows ionization as low as 13 volts; he found two potentials at 12.5 and 16.1 volts. Studying low voltage arcs in oxygen, Lockrow and Duffendack[13] found critical potentials at 16.1 and 19.5 volts. The lower, that at which the arc broke, they ascribed to the formation of O_2^+; the upper, a critical potential for changes in the spectrum, was attributed to the formation of O_1^+ by the process $O_2=O_1^++O+\epsilon$. The lower potential of Mackay and the upper one of Lockrow and Duffendack are thus in good agreement with those found above for the formation of O_2^+ and of O_1^+ respectively.

From the evidence based on the magnetic and chemical properties of oxygen, G. N. Lewis[14] has given :ö: :ö: as the schematic structure of the oxygen molecule—a molecule then with two unpaired electrons. Now Saunders[15] has pointed out that atoms with unpaired electrons have low ionizing potentials, the tendency of electrons to pair resulting then in the observed alternation in the value of the ionization potentials of the elements with increase in atomic number; Mulliken[16] and Birge[17] have suggested an analogy between the energy levels of atoms and of

[10] See Smyth, Phys. Rev. **25**, 452 (1925).

[11] For a summary of these see Compton and Mohler, Bull. Nat. Res. Council, vol. 9, part 1, *Critical Potentials*.

[12] Mackay, Phys. Rev. **24**, 319 (1924).

[13] Lockrow and Duffendack, Phys. Rev. **25**, 110 (1925).

[14] G. N. Lewis, Chemical Reviews **1**, 231 (1924); J. Am. Chem. Soc. **46**, 2027 (1924).

[15] Saunders, Science **59**, 47 (1924).

[16] Mulliken, Phys. Rev. **26**, 561 (1925).

[17] Birge, Nature **117**, 300 (1926).

molecules. It might therefore be anticipated that, because of the two unpaired electrons in the oxygen molecule, the ionization potential of oxygen would be lower than that of nitrogen. Experiment shows this to be the case. It might be expected, too, that oxygen, containing, as it does, three distinct kinds of electrons (bonding, unpaired—non-bonding, and paired—non-bonding) would have two ionization potentials in addition to that for the disruption of the molecule. Now Mackay[12] did find two lower ionization potentials. From this point of view the lower one (12.5 volts) perhaps corresponds to the ejection of an unpaired electron, the upper one (16.1 volts) to the ejection of a paired—non-bonding electron.*

The difference in the processes by which the atomic ions are formed in the ionization of oxygen and of nitrogen suggests correlating these processes with the recent theory of Franck[18] on the dissociation of molecules by the absorption of radiation. Franck assumes that the absorption of a light-quantum results only in an electron transition and that the nuclear separation remains unchanged at the moment of this transition. With the electron in a new energy level the nuclei then find themselves held together by a different binding energy; this different binding energy gives rise to a different amplitude and hence, a different frequency of vibration. He further assumes that there is a limiting distance of approach of the nuclei, beyond which there will be sufficient repulsion to cause disruption, and as the binding force is weakened, i. e., as the equilibrium positions of the nuclei are more widely separated, this limiting distance of approach becomes greater. If then, as the result of an electron transition, the equilibrium positions of the nuclei are suddenly at a greater distance apart than before, the two nuclei may, at the moment of transition, be beyond the limiting distance of approach and hence disruption will follow. Dymond[19] found this to be the case in iodine, and Birge and Sponer[20] have recently found this to be true of oxygen as well. Professor Birge has informed us that ionized oxygen in the excited state corresponding to about 20 volts energy has a much slower vibration frequency than

* The O_2^+ (20 volts) which spontaneously breaks down into O and O^+ may be regarded as being either an O_2^+ with a remaining electron excited, or an O_2^+ with a different kind of electron (bonding) removed from that produced at 13 volts. In our work on nitrogen[3] the latter view was assumed, while Sponer has since suggested the former. The evidence favoring Dr. Sponer's suggestion is that but one series limit for the electron levels in nitrogen is known. Naturwiss. **13**, 275 (1926).

[18] J. Franck, Trans. Faraday Soc., 1925.

[19] Dymond, Zeits. f. Physik **34**, 553 (1925).

[20] Birge and Sponer Abst. 13, Stanford Meeting; Birge, Abst. 14, *ibid.*; Birge and Sponer (to be published in full).

the normal state; this means that the equilibrium positions are at greater nuclear separation. Very probably then, the mechanism assumed by Franck for dissociation by absorption of radiation and by electron impact applies to this case of dissociation. Nitrogen does not show this same difference in vibration frequencies in the normal and ionized states, so that the nitrogen nuclei would not be beyond the limit of closest approach in the N_2^+ ion produced at 24 volts[3] and no spontaneous dissociation would follow.

It may be recalled that in the case of hydrogen[2] and nitrogen[3] the measurement of the ionization potentials for the formation of H_1^+ and N_1^+ respectively could give only upper limits to the heats of dissociation as the atomic ions are formed by secondary processes. In the case of oxygen, however, since O_2^+ is formed by a direct process, the heat of dissociation of oxygen can be calculated unambiguously. For

$$O_2 = O_1^+ + O + \epsilon; \ 20 \text{ volts} \quad (3)$$
$$O = O_1^+ + \epsilon \quad ; \ 13.5 \text{ volts}^{21} \quad (4)$$

which, by subtraction, gives 6.5 volts or 150,000 calories per mol as the heat of dissociation of oxygen. The possible limits for the heat of dissociation of oxygen as set by critical potential measurements have been discussed by Wulf. [22] Owing to a lack of interpretation of those measurements the limits were rather wide—56,400 and 137,400 cal. per mol. The latter agrees within the experimental error with that found above, and the new limits are set by the limits of accuracy of the determination of the ionization potential. No claim is made for great accuracy in the above critical potential measurements. As previously done we might make a conservative estimate of ± 1 volt, although the maximum deviation of our few values from the above means was 0.4 volt. Born and Gerlach,[23] following a suggestion of Franck and Grotrian, and utilizing Warburg's[24] measurement of the long wave-length limit for the formation of ozone, have calculated the heat of dissociation of oxygen to be 162,000 cal. per mol. Since we obtained our value of 6.5 volts, Birge and Sponer have calculated the heat of dissociation from data derived from band-spectra. The concordance of their value of 7.05 ± 0.03 volts ($162{,}600 \pm 700$ cal.) with those of two such very different experimental methods suggests strongly

[21] Hopfield, Phys. Rev. **21**, 710 (1923).
[22] Wulf, J. Am. Chem. Soc. **47**, 1944 (1925).
[23] Born and Gerlach, Zeits. f. Physik **5**, 433 (1921).
[24] Warburg, Sitzungsber. d. preus. Akad. d. Wiss., Math-phys. Kl. 1914, p. 872.

the fundamental correctness of the assumptions underlying these methods.

Throughout the above paper it has been tacitly assumed that the ion of $m/e=16$ was O_1^+ and not O_2^{++}. It is now seen that the chief justification for this assumption is that it is consistent with the spectroscopic observations of Lockrow and Duffendack,[13] and that it leads to a consistent value for the heat of dissociation of oxygen. Professor Birge has sufficient data to assure us that the energy of formation of O_2^{++} is greater than 20 volts. The ion appearing at 20 volts can therefore be only O_1^+.

In conclusion, the authors wish to express their thanks to Prof. R. T. Birge and Dr. H. Sponer of the Department of Physics for making available a large amount of unpublished results, as well as for their kindly interest in the progress of this work.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
March 23, 1926.

ANALYSIS OF POSITIVE IONS EMITTED BY A NEW SOURCE

By Henry A. Barton,* Gaylord P. Harnwell, and C. H. Kunsman.

Abstract

Certain iron oxide crystals containing about one percent of some alkali metal or alkaline earth have been developed by the Fixed Nitrogen Research Laboratory for use as catalysts in the synthesis of ammonia. It has been found that these substances also have great experimental utility as constant and abundant emitters of positive ions. The writers have tested various methods of mounting and heating these emitters. They have also analyzed their emission by the use of a mass spectrograph which has been described by Smyth. Separate catalyst samples containing respectively Na, K, Rb, Cs, Mg, Ca, and in one case both Ba and Sr have been shown in this way to emit only the corresponding singly charged positive ion. No doubly charged ions were observed, nor any ions of the other elements composing the catalysts. The alkali metal ions were emitted at lower temperatures than the alkaline earth ions. Particularly in the case of the latter, a preliminary treatment consisting of reduction at red heat in an atmosphere of hydrogen increased the emission.

Emission from hot platinum was also observed consisting of Na^+ and K^+ ions. This was a surface effect and diminished rapidly with time.

Introduction

Kunsman[1] has described a new and convenient source of positive ions which is finding many uses in experimental research. This source consists of heated crystal granules of certain catalysts developed for the synthesis of ammonia at the Fixed Nitrogen Research Laboratory in Washington. Briefly, these consist of a fused mixture of iron oxide and about one percent of an oxide of an alkali metal or alkaline earth, with sometimes the addition of about one percent of aluminium oxide. The method of preparation[2] and an x-ray analysis[3] of the crystals have recently been published.

When the crystals are heated they emit positive ions in large numbers. If they are further prepared by reduction in an atmosphere of hydrogen and then glowed and degassed in a good vacuum, the positive ion current is quite constant. This current in a high vacuum is a function of temperature and accurately obeys Richardson's equation, $I = AT^{1/2}\epsilon^{-b/T}$ for thermionic emission. More recently Kunsman has

* National Research Fellow, Harvard University.

[1] Kunsman, Science, **62**, 269 (1925).

[2] Larson and Richardson, J. of Ind. Chem. **17**, 971 (1925).

[3] Wyckoff and Crittenden, J. Am. Chem. Soc. **47**, 2866 (1925).

considerably extended his investigation of the thermionic properties.[4]

For precise experimental work using this type of positive ion source, it is, of course, highly important to have full knowledge of the nature and homogeneity of the ions emitted. The present paper describes a positive ray analysis undertaken primarily to answer this question. Seven samples were investigated, being iron oxide crystals as described, and containing, respectively, caesium, rubidium, potassium, sodium, magnesium, calcium, and, in one sample, both barium and strontium.

Apparatus

The experimental arrangement[5] is shown schematically in Fig. 1. Some of the sample source under investigation was mounted on a platinum filament at F, this being supported by the leads (not shown)

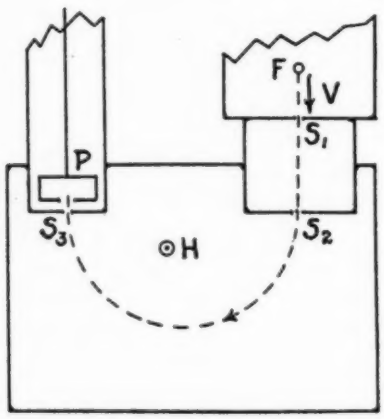


Fig. 1. Apparatus.

which carried the heating current. The arrangement of slits, electric and magnetic fields is obvious. P was connected to a Compton electrometer. A mass spectrum was obtained by progressively varying V with H constant and observing the electrometer current. In most of the experiments the field strength was about 4400 gauss and V was varied from 0 to 400 volts. S_2 and S_3 were 6 cm apart. A vacuum of better than 10^{-4} mm of Hg was maintained throughout. The best resolution obtained was not sufficient to separate isotopes, but easily distinguished ions of elements in different rows of the periodic table.[6]

[4] Kunsman, to be published shortly.

[5] The tube used was that described by Smyth, Phys. Rev. **25**, 452 (1925), except that two of the electrodes were removed and the evacuating arrangements simplified.

[6] In two runs the potassium peak indicated by its shape that little more resolving power would have been needed to separate the two isotopes at 39 and 41.

In the course of the experiments four different methods of mounting and heating the catalysts were used. At first the tube was so oriented that the filament and slit S_1 were in the same horizontal plane, a trough with an open side towards S_1 could be used. Later the arrangement was changed so that F was above S_1 as shown in Fig. 1. It was then necessary to turn the trough open side up so as not to spill out the granules and provide small perforations in the bottom for the emission. This method proved less satisfactory, so a narrow, twisted strip of platinum was next mounted and covered as completely as possible with a coating of pulverized catalyst granules. The coating was put on with the aid of paraffin as a vehicle in the same manner as is frequently used in the preparation of oxide coated filaments, the paraffin being vaporized by heating, once the active material is in place. This method has the valuable advantage of providing a large emitting surface.

Although the last mentioned method proved very satisfactory for the alkali metal catalysts, a fourth type of filament was used for those containing alkaline earths. Difficulty was found in coating strip filaments with these. They did not seem to adhere as well as the alkali metal samples. This resulted in an uneven coating so that the heating along the filament was not uniform. Owing to the greater temperatures which had to be used to obtain emission in these cases, this difficulty shortened the life of the filaments considerably. The type of filament finally adopted consisted of a thin-walled platinum tube with small perforations in the side toward S_1 to allow ion emission. This was filled with a finely granulated sample of catalyst and the ends squeezed together to keep it in. The alkaline earth and rubidium samples were investigated in this way.

All of the filaments were less than 1 cm in length. They required heating currents ranging from 4 or 5 amps. for the twisted strip type to 15 amps. for the tube type.

Alkali Metals

Mass spectra of the emission from the four alkali metal samples are given in Fig. 2. The ordinates, representing electrometer current, are arbitrary and not comparable from one curve to another. This arises from the fact that the electrometer current depended upon the pressure of gas in the path of the ions (which caused scattering), the effective area of the granules mounted on the filament, and the exact position of the latter. It was not possible to have these always the same.

Furthermore no means were available for measuring the temperature of the filament.

Caesium (*132.8*). The mass spectrum of the caesium sample shows a large diffuse peak corresponding to Cs^+ ions. The resolution of the apparatus is not as good for heavy ions as for light, which chiefly accounts for the width of this peak. It is also characteristic of the apparatus that the peak shades off toward lower m/e values. It is quite possible, however, that the shoulder just above 80 is due to Rb^+ impurity. The curve was extended below 50 and very large K^+ and Na^+ peaks observed. These have not been indicated in the figure

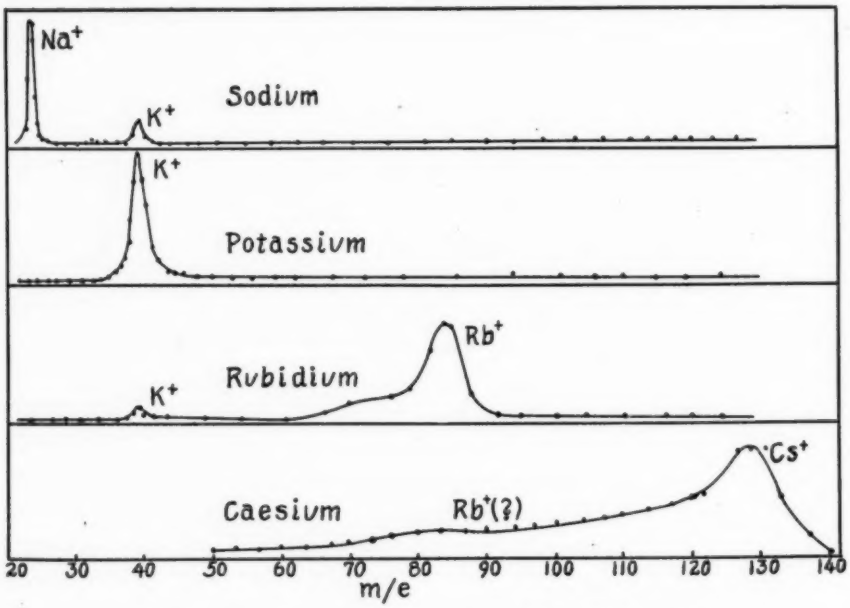


Fig. 2. Mass spectra of catalysts containing alkali metals.

because it was later definitely established that they came from the platinum filament itself or from a contamination on it from previous samples. Later a new filament was prepared and tested for K^+ and Na^+ before being coated. After this had been coated with some of the caesium sample, a large Cs^+ peak was obtained with little or no K^+ or Na^+.

Rubidium (*85.5*). The emission from this sample was at first small. After reduction by the same method as will be described in connection with the alkaline earth samples it was much better. The curve in Fig. 2 shows a run then taken, the only impurity being a small amount of K^+.

Potassium (*39.1*). The curve shows remarkable freedom from the other alkali metals as impurities.[7]

Sodium (*23.0*). The curve of this sample shows a very sharp principal peak indicative of the resolution obtainable at the lower end of the m/e scale. The K impurity was much more pronounced when the filament was first heated, then diminished rapidly and was still diminishing when the curve was taken. It was probably due chiefly to emission from the platinum, of which more will be said below. In the portion of the m/e scale through which a broken line has been drawn, rates of electrometer deflection were not timed. They were observed carefully, however, and it may be said definitely that no peaks comparable with the K^+ peak were to be found.

Alkaline Earths

Mass spectra obtained from the catalysts containing the alkaline earths are shown in Fig. 3. As mentioned above, it was found necessary to go to higher temperatures to obtain characteristic positive ion emission from these substances. Also the emission was greatly increased if they were submitted to a preliminary period of reduction. This was done by mounting the filament in an atmosphere of hydrogen at about 1 cm pressure and heating at a redness just above visibility for about 24 hours. It is possible that the continued heating altered the condition of the sample as well as reducing the surface. Samples so prepared were found to emit singly charged positive ions of the alkaline earths, but in almost all of the runs, certain impurities of sodium and potassium were found which never completely disappeared with time.

In Fig. 3 two characteristic curves are plotted for each sample. The curve marked I represents one of the first runs, which was taken at a low temperature. The procedure then was to increase the temperature and, after a certain lapse of time, to allow conditions to reach a possible state of equilibrium, another run was taken. This process was continued until the filament burned out or the leads became dangerously hot. The curve marked II is a representative run taken at the highest temperature obtainable. The comparative temperatures were judged entirely by the current passing through the filament. The time elaspsing between runs I and II varied with the samples but was of the order of several hours. The impurities were found to decay very rapidly with time, probably exponentially. The ordinates of the curves

[7] This curve was taken some months before the rest of the work was done. It was mentioned by Kunsman. (Ref. 1.)

of the different substances are again not comparable because the conditions, particularly the temperatures, were not identical.

Barium (137.37) and Strontium (87.63). Curve I shows no evidence of anything but Na^+ and K^+ which were evidently present as impurities, probably, to a very large extent, coming only from the platinum. Curve II shows a very small peak at K^+, a distinct but very broad peak at Sr^+, and a very large peak at Ba^+. The Sr^+ peak is surprisingly small relative to the Ba^+ peak, the reason for this being uncertain. No evidence of Sr^{++} or Ba^{++} was found.

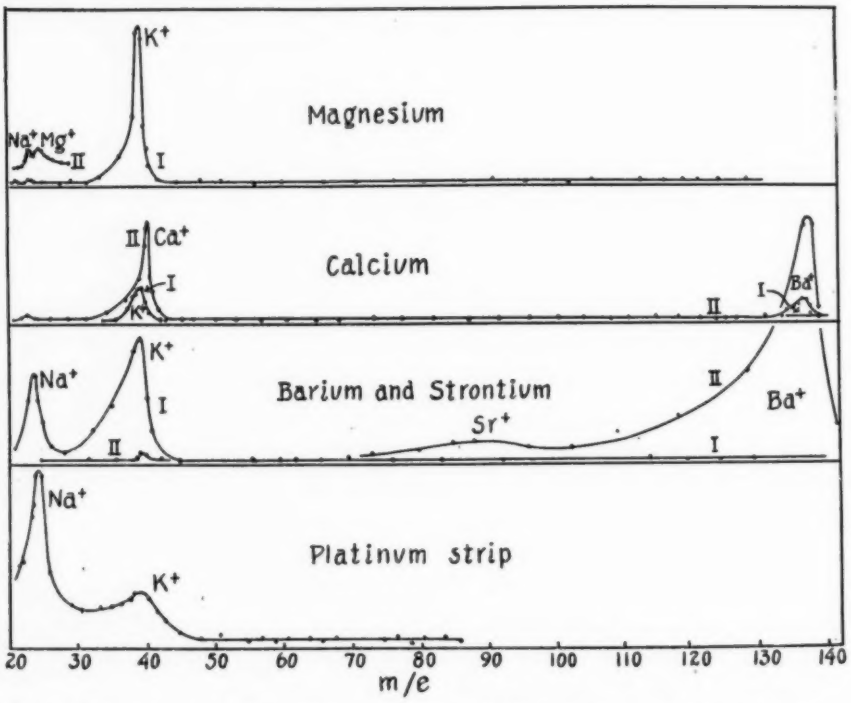


Fig. 3. Mass spectra of catalysts containing alkaline earths and of bare platinum.

Calcium (40.07). Curve I shows only a K^+ peak. Curve II shows a very slight Na^+ peak, a large peak for Ca^+ and a peak of about one-third the height of Ca^+, for Ba^+. An incomplete run at a slightly higher temperature was obtained in which the Ba^+ peak rose relatively to the Ca^+ peak. Again no evidence of Ca^{++} or Ba^{++} was obtained.

The rather small shift of the principal peak toward higher m/e in passing from low to high temperatures is perhaps not sufficient in itself to justify the statement that the K^+ emission is replaced by Ca^+. There is good reason to believe, however, that this shift is genuine.

Furthermore, other evidence is quite in favor of the existence of Ca^+ emission. For example, this 'shifted' peak remained approximately constant at any given temperature, whereas in all cases where K^+ was present as an impurity, the peak corresponding to it diminished rapidly with time. These facts together with the undoubted emission of the other alkaline earths are considered conclusive evidence for the existence of Ca^+ emission.

Magnesium (*24.32*). Curve I shows a small Na^+ peak and a very large K^+ peak. In the following runs the K^+ fell in comparison with the Na^+ peak and they both dropped off with time at constant temperature. In the run at the highest temperature obtained the Na^+ and Mg^+ peaks were distinctly resolved. The filament burned out before the region containing the K^+ peak could be examined. In subsequent runs the filament never lasted long enough at a temperature sufficient to produce Mg^+ to examine in detail the other regions, but no evidence of anything but a K^+ peak was discovered. Voltages high enough to cover the region where Mg^{++} would lie were not used.

Ions From Platinum

The first few runs with the potassium sample of catalyst showed sodium ions also present. Subsequent runs using the same filament charged with caesium catalyst showed sodium and potassium in addition to caesium ions. The filament was taken out and chemically cleaned. It was then replaced and found to emit sodium and potassium ions as before but the caesium had been quite removed. The filament was taken out a second time and heated white hot in a blast flame to volatilize any traces of alkali metals left on the surface by the catalyst samples. In spite of this the sodium and potassium ions still persisted. A new platinum strip was then mounted and this too was found to emit sodium and potassium ions. The first curve obtained in this case is given in Fig. 3.

No particular study was made of this emission of ions by the platinum itself. It was observed however that an increase in the temperature of the strip always produced increased ion emission, particularly of potassium, and that this very quickly diminished if the temperature were then kept constant. It was partly due to the latter fact and partly to care in covering up as much of the platinum surface as possible with catalyst that the sodium, potassium, and rubidium curves show little evidence of this emission.

More extended investigations of the emission from hot platinum have been made by others. A summary of these investigations, together

with certain conclusions drawn from the results, has been given by Richardson.[8] The above observations, as far as they go, confirm these conclusions. This is particularly the case as regards the constitution of the ions emitted by platinum, for the present resolving power appears to be better than that of any apparatus heretofore used to study the phenomenon.

Discussion

The mass spectra given in Figs. 2 and 3, together with the circumstances of their production, lead to the conclusion that the only ions emitted in each case were those of the alkali metal or alkaline earth present in the catalyst. The much more abundant iron and oxygen atoms did not appear as ions, nor did aluminium in the catalysts where it too was present. It is interesting that the alkaline earth ions, like those of the alkali metals, were only singly charged, in spite of their possession of two loosely bound valence electrons.

The evidence does not give sufficient basis for much discussion of the mechanism of emission. Very roughly it appeared in the case of the alkaline earths that the lighter elements required higher temperatures to produce emission. Certainly these elements required considerably higher temperatures than the alkali metals. The difficulty seems to vary in the same direction as the ionizing potentials. This may account for the difference in the heights of the barium and strontium peaks.

The chief distinction between these emitters and others is, of course, their constancy and relative inexhaustibility. There is evidently something about their structure which permits the ion-forming atoms to diffuse readily and abundantly to the surface. In most other cases the ion emission rapidly falls off as the supply or at near the surface becomes exhausted.[8]

The authors are indebted to members of the staff of the Fixed Nitrogen Research Laboratory and also to Professors K. T. Compton and H. D. Smyth for valuable suggestions and indispensable assistance.

Palmer Physical Laboratory,
Princeton University,
Princeton, N. J.
January 29, 1926.

[8] Richardson, The Emission of Electricity from Hot Bodies, Chaps. VI and VII.

ON THE THEORY OF ELECTROSTATIC ALTERNATORS

By A. W. Simon[1]

Abstract

A more elegant method than that previously given for the solution of the equations involved in the theory of electrostatic alternators is given, and illustrated by application to an electrostatic alternator of eight inductors and eight carriers, in which each carrier as it comes in front of an inductor is connected to the next following inductor by means of a brush and insulated arm. The method can be extended to the solution of electrostatic alternators of m carriers and m inductors, where each carrier is connected to the inductor next following, also where each carrier is connected by means of brushes properly placed to the pth inductor following. It may also be applied to electrostatic alternators with m inductors and $2m$, $3m$, or $4m$ carriers, and to electrostatic alternators of the Wimshurst type. With regard to the eight inductor alternator it is shown that three waves travel around the machine with periods corresponding to the time of 2 revolutions, 1 revolution, and 2/3 revolutions. The amplitude factor for each wave per eighth revolution is calculated approximately. Finally the effect of the initial conditions (potentials) on the action of the machine is discussed. It is shown that the potentials of the inductors of the machine eventually lag $\pi/4$ behind each other.

THE quantitative theory of a four inductor alternator of the type to be discussed in the present work has already been given,[2] and a general method of solution of alternators of this type outlined.[3] Since the publication of this work, however, it has been possible to develop a much more elegant method of solving the equations involved in the theory of these machines, and our present work is concerned both with an exposition of this method as well as a discussion of the physical interpretation of the results obtained by its application.

As the subject of our analysis we shall take an eight inductor electrostatic alternator, and present the theory of this machine in a form which admits of ready extension to alternators of this type with any number of inductors.

The machine studied is represented diagrammatically in Fig. 1. It consists of eight fixed inductors, and eight revolving carriers, and operates in a manner easily seen from the figure. The inductors are assumed to be identical in shape and symmetrically mounted, and the same is assumed to apply to the carriers.

[1] National Research Fellow.
[2] A. W. Simon, Phys. Rev. **25**, 368 (1925).
[3] A. W. Simon, Phys. Rev. **26**, 111 (1925).

By exactly the same method as was employed in the case of the four inductor alternator already cited,[4] it can be shown that the potentials of the inductors after $(n+1)$ and n cycles satisfy a set of equations of which the left members take the form:

$$\begin{array}{llllllllllllllll}
aV_0(n+1) & + & hV_1(n+1) & + & gV_2(n+1) & + & fV_3(n+1) & + & eV_4(n+1) & + & dV_5(n+1) & + & cV_6(n+1) & + & bV_7(n+1) & \\
b & " & +a & " & +h & " & +g & " & +f & " & +e & " & +d & " & +c & " \\
c & " & +b & " & +a & " & +h & " & +g & " & +f & " & +e & " & +d & " \\
d & " & +c & " & +b & " & +a & " & +h & " & +g & " & +f & " & +e & " \\
e & " & +d & " & +c & " & +b & " & +a & " & +h & " & +g & " & +f & " \\
f & " & +e & " & +d & " & +c & " & +b & " & +a & " & +h & " & +g & " \\
g & " & +f & " & +e & " & +d & " & +c & " & +b & " & +a & " & +h & " \\
h & " & +g & " & +f & " & +e & " & +d & " & +c & " & +b & " & +a & "
\end{array}$$

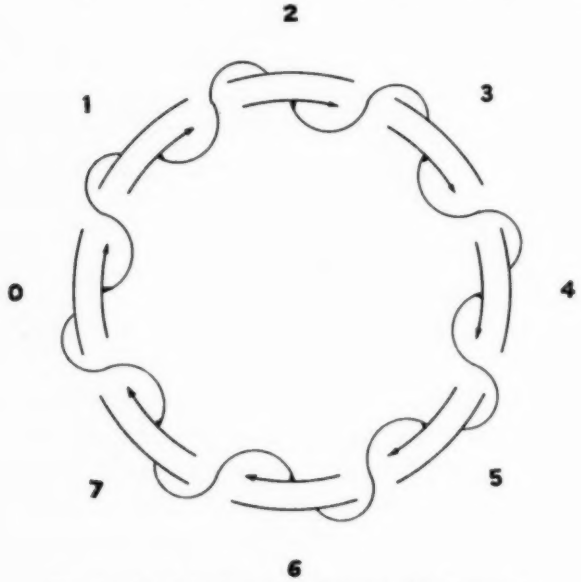


Fig. 1. An eight inductor electrostatic alternator.

and the right members take exactly the same form except that the coefficients a, b, c, etc. are replaced by a', b', c', etc. respectively, and the argument $(n+1)$ of the functions $V_s(n+1)$ is replaced by n.

I. General Solution of the Voltage Equations

Of fundamental importance for the mathematical solution of these equations is the following matrix, in which ω_j stands for the eighth root of unity corresponding to the amplitude of $j2\pi/8$.

$$\begin{array}{cccccccc}
\omega_0^0 & \omega_0^1 & \omega_0^2 & \omega_0^3 & \omega_0^4 & \omega_0^5 & \omega_0^6 & \omega_0^7 \\
\omega_1^0 & \omega_1^1 & \omega_1^2 & \omega_1^3 & \omega_1^4 & \omega_1^5 & \omega_1^6 & \omega_1^7 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\omega_7^0 & \omega_7^1 & \omega_7^2 & \omega_7^3 & \omega_7^4 & \omega_7^5 & \omega_7^6 & \omega_7^7
\end{array} \qquad (2)$$

[4] A. W. Simon, Phys. Rev. **24**, 690 (1924).

For the purpose of the following work we shall number the rows and columns from 0 to 7, instead of from 1 to 8, as is the usual custom.

If we multiply the equations in order by the elements in the jth row of this matrix, and add, we obtain an equation of the form:

$$[a\omega_j^0+b\omega_j^1+c\omega_j^2+\cdots+h\omega_j^7][\omega_j^0V_0(n+1)+\omega_j^1V_1(n+1)+\cdots]=$$
$$[a'\omega_j^0+b'\omega_j^1+c'\omega_j^2+\cdots+h'\omega_j^7][\omega_j^0V_0(n)+\omega_j^1V_1(n)+\cdots]$$

the solution of which is obviously:

$$[\omega_j^0V_0(n)+\omega_j^1V_1(n)+\cdots]=\frac{[a'\omega_j^0+b'\omega_j^1+\cdots]^n}{[a\omega_j^0+b\omega_j^1+\cdots]^n}$$
$$[\omega_j^0V_0(0)+\omega_j^1V_1(0)+\cdots] \quad (3)$$

and, if we do this for every row, (i. e., if we let j run through the sequence of values 0, 1, $\cdots$ 7) we obtain eight simultaneous linear equations, the left members of which involve the functions $V_s(n)$ and the ω's, and in which the matrix of the coefficients of the left members is exactly the matrix (2). By elimination from this set we can then obtain each of the functions $V_s(n)$ in terms of the quantities $V_s(0)$ and the quantities $[a'\omega_j^0+b'\omega_j^1+\cdots]^n/[a\omega_j^0+b\omega_j^1+\cdots]^n$.

Now the matrix (2) has two important properties which allow us to carry out the process of elimination very easily. (1) If we examine the sum of the quantities in any column, we note that it is the sum of like powers of the roots of the algebraic equation $x^8-1=0$, and from the formula for the sum of like powers of the roots of an algebraic equation, it follows directly that the sum of the quantities in every column of the matrix (or row, if we replace every element of the form of $\omega_p{}^q$ by $\omega_q{}^p$), except the first, is zero. (2) If we divide each row through by the factor which will make the elements in the sth column all unity, the resulting matrix can be obtained from the matrix (2) by s cyclic permutations of the columns of the matrix (2), and has the property that the sum of the coefficients in every column except the sth is zero.

To solve for any $V_s(n)$ then we have merely to divide the equations (3) through by such factors as will make the elements in the sth column of the matrix (2) all equal to unity, and then add the resulting equations.

Accordingly, we have as the general formula for $V_s(n)$:

$$8V_s(n)=\sum_{j=0}^{7}[\omega_j^0V_0(0)+\omega_j^1V_1(0)+\cdots][a'\omega_j^0+b'\omega_j^1+\cdots]^n/\omega_{sj}$$
$$[a\omega_j^0+b\omega_j^1+\cdots]^n \quad (4)$$

where ω_{sj} is the element in the sth column and jth row of the matrix (2).

Now while each term of this sum is complex, the sum itself is real, for we can group the complex terms into pairs of conjugate terms, such that the imaginary parts will cancel out in the sum.

This is readily seen from the matrix (2) if in addition we note that each of the expressions in brackets in formula (4) is obtained by combining a sequence of eight quantities, (namely the sequences $V_0(0)$, $V_1(0), \cdots, V_7(0)$; $a', b', \cdots, h'$; and $a, b, \cdots, h$) with the elements in any row of the matrix. As pairs of rows which give rise to conjugate terms we have 1,7; 2,6; and 3,5. The rows 0,4, it may be pointed out, give rise to real terms. For the purpose of our further calculations it is convenient to rewrite Eq. (4) in another form. If namely we put:

$$[\omega_j^0 V_0(0)+\omega_j^1 V_1(0)+\cdots]=[A_j(0)+iB_j(0)]=R_j(0)[\cos\Delta_j+i\sin\Delta_j]$$
$$[a'\omega_j^0+b'\omega_j^1+\cdots]=[\alpha_j'+i\beta_j']=\sigma_j'[\cos\varphi_j'+i\sin\varphi_j']$$
$$[a\omega_j^0+b\omega_j^1+\cdots]=[\alpha_j+i\beta_j]=\sigma_j[\cos\varphi_j+i\sin\varphi_j]$$
$$\omega_{sj}=\cos\partial_{sj}+i\sin\partial_{sj}$$

and, further, let $\rho_j=\sigma_j'/\sigma_j$ and $\theta_j=\varphi_j'-\varphi_j$, we can rewrite Eq. (4) as:

$$8V_s(n)=\sum_{j=0}^{7}[A_j(0)+iB_j(0)]\rho_j^n[\cos(n\theta_j-\partial_{sj})+i\sin(n\theta_j-\partial_{sj})]$$

II. Particular Solutions of the Voltage Equations

For various assumed initial conditions, i. e., sets of values of the quantities $V_s(0)$, the general solution reduces to simple forms. In particular consider the sets of values given by:

$$V_s(0)=E(0)\cos(s-p)k2\pi/8 \tag{5}$$

where s, p, and $-k$, take the values $0, 1, 2, \cdots, 7$. We then have for $A_j(0)$ and $B_j(0)$, respectively:

$$A_j(0)=E(0)\sum_{s=0}^{7}[\cos(s-p)k2\pi/8][\cos sj2\pi/8],$$

$$B_j(0)=E(0)\sum_{s=0}^{s=7}[\cos(s-p)k2\pi/8][\sin sj2\pi/8].$$

Now from the fact that $\sum_{s=0}^{7}\omega_p\omega_s^r=0$, or $8\omega_p$, respectively, according as $\pm r\neq 0$, 8, 16, etc., or as $\pm r=0$, 8, 16, etc., and from trigonometry, it is possible to prove readily the following theorem:

Theorem I. For any given k such that $-k\neq 0$ or 4, we have $A_j(0)=0$ and $B_j(0)=0$, for every value of j except $j=-k$ and $j=8+K$; for $j=-k$ and $j=8+K$, $A_j(0)=4E(0)\cos(-pk)2\pi/8$ and $B_j(0)=4E(0)\sin$

$(-pk)2\pi/8$; while for $k=0$ or -4, $A_j(0)=0$ and $B_j(0)=0$, for every value of j except 0 or $+4$; finally for $kj=0$ or -4, $A_j(0)=8E(0)\cos(-pk)2\pi/8$, $B_j(0)=0$.

III. Physical Interpretation of the Results

For the physical interpretation of the results we need to know the relative magnitudes of the quantities ρ_j and θ_j. These are obtained by substituting in the formulas for ρ_j and θ_j, the values of the quantities a, a', b, b', etc. in terms of the coefficients of capacity and coefficients of induction of the elements of the machine in that configuration at which the carriers just break contact with the brushes. In order to calculate exactly the various values of ρ_j and θ_j we would require the numerical values of these coefficients. It is, of course, impossible to calculate these. To complete the analysis of any machine it would be necessary to actually measure them. However, we can gain some idea of the relative magnitudes of the ρ's and θ's involved, if we make the same assumptions as were made in the case of the four inductor alternator, namely, that the inductors nearly completely surround the carriers and that the inductors are relatively far apart. Under these conditions we can calculate the following set of values for the ρ's and θ's involved.

j	$\tan\theta$	θ	ρ
0	0	0	1
1, 7	$\sqrt{2}-1$	$\pi/8$	$\sqrt{2}/\sqrt{2-\sqrt{2}}$
2, 6	1	$\pi/4$	$\sqrt{2}$
3, 5	$\sqrt{2}+1$	$3\pi/8$	$\sqrt{2}/\sqrt{2+\sqrt{2}}$
4	0	0	0

The values obtained on the basis of these assumptions are really ideal values which in practice we can only approximate. Nevertheless, they correctly indicate the relative magnitudes of the quantities in question, so that for the purpose of our further discussion we shall assume:

$$\rho_0=1,\ \rho_1>\rho_2>1,\ \rho_3<1,\ \rho_4<1;$$
$$\theta_0=0,\ \theta_1\doteq\pi/8,\ \theta_2\doteq\pi/4,\ \theta_3\doteq 3\pi/8,\ \theta_4=0.$$

The phase angles ∂_{sj}, on the other hand, are independent of the capacities involved in the machine, and are readily determined from the matrix (2). In particular, we have

$$\partial_{s0}=0,\ \partial_{s1}=s\pi/4,\ \partial_{s2}=s\pi/2,\ \partial_{s3}=s3\pi/4,\ \partial_{s4}=s\pi.$$

With all these relations before us we can inquire as to the action of the alternator. We see that in general the action of the machine may be described by asserting that three potential waves of different

periods travel around the machine, two of which continually increase in amplitude ($\rho>1$) and one of which continually decreases in amplitude ($\rho<1$). Furthermore, eventually, one only of these waves will be perceptible, the others becoming either vanishingly small or negligible in comparison. The wave in question is that corresponding to ρ_1 and θ_1, for we have, for n large,

$$V_s(n)=R_1(0)\rho_1^n\cos\,(n\theta_1+\Delta_1-s\pi/4)\ .$$

However, the action of the alternator will depend, theoretically at least, very markedly on the initial conditions. For example, if we choose the original potentials so as to satisfy the set of values given by equation (5); that is, if we adjust the original potentials so that there will be a difference of phase of $k2\pi/8$ between each pair of successive inductors and if, furthermore, we put the maximum potential on the pth inductor, then only that wave corresponding to $j=-k$ will be present.

If we let $-k$ vary from 0 to 4 and apply Theorem I, we obtain a number of interesting special cases, which it should be possible to verify experimentally.

(1) $k=0$, $V_s(0)=E(0)=\text{const.}$ The original potentials are all the same. For this case, if in addition we note that it can be shown by the method of a previous paper,[4] $\rho_0\equiv 1$, no matter what the capacities involved in the machine are, as long as it is symmetrical, we have for every n from 0 to ∞ : $V_s(n)=E(0)=\text{const.}$, that is to say, no change takes place, as we might expect also from qualitative considerations.

(2) $-k=1$, $V_s(0)=E(0)\cos(s-p)(-\pi/4)$. The corresponding solution is, for every n from 0 to ∞ :

$$V_s(n)=E(0)\rho_1^n\cos\,[n\theta_1-(s-p)\pi/4]\ .$$

Under these conditions the potential will reverse approximately every revolution, and the machine will build up very rapidly.

(3) $-k=2$, $V_s(0)=E(0)\cos(s-p)(-\pi/2)$. The solution in this case is given by

$$V_s(n)=E(0)\rho_2^n\cos\,[n\theta_2-(s-p)\pi/2]\ .$$

The potential now reverses approximately every half revolution, but the machine does not build up as rapidly as in case (2), since $\rho_2<\rho_1$.

(4) $-k=3$, $V_s(n)=E(0)\rho_3^n\cos[n\theta_3-(s-p)3\pi/4]$. The potential reverses approximately every third of a revolution, but the potentials continually decrease, ($\rho_3<1$), and eventually become vanishingly small. In practice they would very likely decrease until the ever-present contact e.m.f.'s took hold and re-excited the machine.

(5) $-k=4$, $V_s(n)=E(o)\rho_4^n\cos[-(s-p)\pi]$. Under these conditions also the potentials would theoretically decrease to zero, or in practice until the contact e.m.f.'s took hold.

IV. Application of the Method to Other Machines

(1) *Multiple Inductor Machines of the type just discussed.* It has already been stated in our opening paragraph that the method of analysis used in the present work for an eight inductor alternator can be applied to a machine of this type with any number of inductors. For the general case of m inductors and m carriers the matrix (2) would be simply a square matrix of the mth order, involving the mth roots of unity. A theorem corresponding to Theorem I could also be set up very easily for the general case. We have merely to note that if ω_j is the mth root of unity which has the amplitude $j2\pi/m$, we have $\sum_{s=0}^{m}\omega_p\omega_s^r=0$ or $m\omega_p$, respectively, according as $\pm r$ is, or as it is not, zero or a multiple of m. This follows directly from the fact that $\sum\omega_s^r$ is the sum of like powers of the roots of the equation $x^m-1=0$.

(2) *Solution for Other Schemes of Connections.* Furthermore, if in the case of the eight inductor system just discussed each carrier is connected not to the next following inductor but to the second, third, or pth one following, we obtain equations of exactly the same form as Eq. (1) except that the constants a, a', b, b', etc. have different values. This means, that the solution is of exactly the same form as before but that the ρ's and θ's have different values, and this again holds in general; namely, that once the solution for one alternator of m inductors is determined for one scheme of connections, the solutions for all other schemes of connections are obtained by assigning to the ρ's and θ's their proper values. Of course, the scheme of connections must be symmetrical and not haphazard.

(3) *Machines with Double the Number of Carriers.* If the eight inductor machine just discussed were built up with 16 carriers instead of 8, the matrix of the coefficients of the voltage equations (sixteen in number) would take the form

$$\begin{matrix} M_1 & M_2 \\ M_3 & M_4 \end{matrix}$$

where each of the matrices M_i is a cyclic matrix of the 8th order. To solve this case, we divide the set of sixteen equations into two sets of eight (the first set involving M_1, M_2, the second M_3, M_4) and apply the method by which Eq. (3) is obtained to each set separately, but

instead of deriving an equation of the form (3), we would now have from the first set one of the form:

$$(a_1+i\beta_1)Z_1(n+1)+(a_2+i\beta_2)Z_2(n+1) = (a_1'+i\beta_1')Z_1(n)+(a_2'+i\beta_2')Z_2(n),$$

and from the second set another of the same type except that the α's and β's have different values. Each of these pairs (and there would be eight such pairs) can be solved by the method of finite differences, as already outlined in previous papers. This method again can be generalized to apply to the alternator with any number of inductors.

(4) and (5) *Machines in which the number of carriers is three or four times the number of inductors.* The method just given for case (3) can be further generalized to apply to the case of 24 and 32 carriers, or in general to the case in which the number of carriers is three or four times the number of inductors. Case (3) above reduces, if the method of finite differences is applied, to the solution of quadratic equations, while the two cases now under consideration reduce to the solution of cubic and biquadratic equations respectively.

(6) *Electrostatic Alternators of the Wimshurst Type.* What has just been said applied also to alternators of the Wimshurst type, since they give rise to equations of exactly the same type as (3), (4), (5).

In general, of course, as the number of inductors and carriers is increased the detailed solution becomes more and more laborious although theoretically it can be carried out. However, it is to be expected that the general features of these machines are not greatly changed by an increase in the number of elements; for example, it is to be expected that doubling the number of carriers will make the voltage wave more continuous without greatly affecting the period of alternation or the transformation ratio.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
January 11, 1926.

A STUDY OF POLARIZATION CAPACITY OVER A WIDE FREQUENCY BAND

By Irving Wolff

Abstract

The polarization capacity of platinum electrodes in sulphuric acid and also of gold electrodes in sulphuric acid has been studied from 200 to 200,000 cycles per second. An alternating current bridge was used to make the measurements in the audible range and a bridge with heterodyne detector for the higher frequencies. If the *relation connecting capacity and frequency* is put in the form $C=C_0/f^P$ where C_0 and P are constants then at the lower frequencies P is nearly equal to .3 while at the higher frequencies it approaches .5. At the same time, the phase angle of the capacity shifts from about 20 to about 40 degrees. Voltage measurements made to determine the *limiting value of the initial capacity* show that it is of the same order of magnitude for alternating current as for direct charge. When *two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell*, the polarization capacity measured by means of either one is independent of the presence of the other.

THE study of polarization capacity phenomena by alternating current methods has taken on a new interest in recent years. The development of alternating current measuring methods during the past decade, particularly the adoption of the vacuum tube for these purposes, has made possible accurate measurements of capacity over a wide range of frequency formerly inaccessible. Predictions which had been made for the action of cells at high frequencies can now be verified or shown in need of modification. On the theoretical side, the views of electrode phenomena which connect polarization with surface reactions afford some very interesting subjects for theoretical investigation.

The first attempt to use frequencies above a few thousand per second for polarization measurements was made by Kruger[1] in 1906. He used a very ingenious method with a damped oscillatory discharge, but not enough points were taken and the frequency range was not sufficiently extended so that very definite conclusions could be drawn. The first serious attempts to get polarization capacity measurements above audible frequencies were made by Merritt[2] and Jolliffe.[3] It is to follow up their work that the present investigation was undertaken.

[1] Kruger, Ann. d. Physik **21**, 301 (1906).
[2] Merritt, Phys. Rev. **17**, 524 (1921).
[3] Joliffe, Phys. Rev. **22**, 293 (1923).

M. Wien[4] had studied the change of capacity with frequency for platinum electrodes in solutions of sulphuric acid at various audible frequencies, and his results, as well as the theorectical explanations given of them by Warburg[5] and Kruger,[6] had led to the expectation that at the higher frequencies the rate of change of capacity with frequency should be lessened, and in fact it was predicted that the capacity would become constant as the frequency was raised. Symbolically, if the relation between P, the back e.f.m. of polarization, and I, the alternating current through the cell is put in the following form (first suggested by Wien[4]) $P=I/C\omega\sin(\omega t-\pi/2+\psi)$, C should tend to become constant and ψ should approach zero as ω becomes greater. Jolliffe has found however that at frequencies from 100,000 to 2,000,000 per second C becomes proportional to $1/\omega^{\frac{1}{2}}$ and ψ is near 45° in the case of gold and for platinum C has been found proportional to $(1/\omega^{\frac{1}{2}}+\text{small const.})$. It is well known that the value of the polarization capacity depends very much on the particular piece of metal used in the cell and even for the same piece varies very much under different conditions. It seemed entirely possible therefore that these discordant results might have been due to the fact that the cells used were different. In order to test the hypothesis a single cell should be carried through both frequency ranges.

Apparatus

A bridge shown in Figs. 1 and 2 was used to make these measurements, a vacuum tube oscillator supplying the alternating current. The arms R_1 R_2 R_3 are non-inductive resistances while a variable inductance is used to balance the capacity in arm 4. Since, as will be shown below, it is necessary to use small potentials across the cell to get the most information from polarization capacity measurements, a three stage amplifier was used in the detector arm of the bridge. In order to get most satisfactory operation of a bridge with an amplifier the Wagner[7] earth connection should be used as shown in diagram. In making measurements, arms 1 and 3 were kept equal. The cell was placed in arm 4 and the variable inductance in this arm and the resistance in arm 2 were adjusted so that the bridge was balanced. A switch was arranged so that a variable capacity box in series with a resistance, wound by the Ayrton method, could be substituted for

[4] Wien, Ann. d. Physik **294**, 37 (1896).
[5] Warburg, Ann. d. Physik **303**, 492 (1899); **311**, 125 (1901).
[6] Kruger, Phys. Zeits. **45**, 1 (1904).
[7] Wagner, Elect. Tech. Zeits. **32**, 1001 (1911).

the cell. It was thus possible to read off directly from this capacity and resistance the capacity and resistance of the cell. The frequency was at the same time easily calculated by noting the value of the vari-

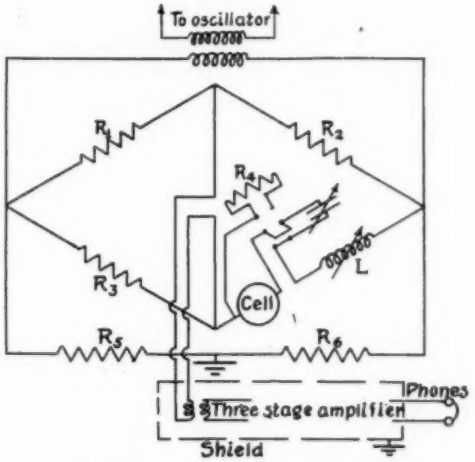


Fig. 1. Audio frequency bridge.

able inductance required to balance this capacity; f then being equal to $1/2\pi\sqrt{LC}$. These calculated values were checked at several points

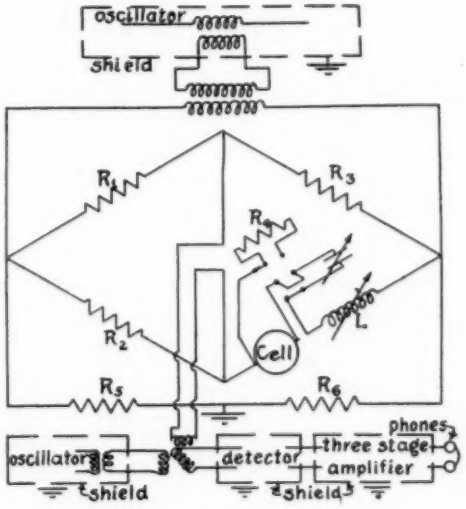


Fig. 2. High frequency bridge.

by means of tuning forks. At frequencies above the audible range a heterodyne beat method of detection was used, the beating current being supplied by a vacuum tube oscillator. This circuit and the de-

tector circuit from the bridge were loosely coupled to a third coil which led to a detector and amplifier. The frequency was measured by means of a S. C. R. Signal Corps wavemeter.

In order to make these measurements strictly comparable with Jolliffe's results the cells he had used (shown in Figs. 3 a "Cell A") were again employed in the first part of this work. The electrodes consisted of either gold or platinum rods of 1 mm radius sealed into glass tubes with DeKotinsky cement and then ground down so that only the cross section was exposed. They were usually placed so as to be between .5 and 1 mm apart.

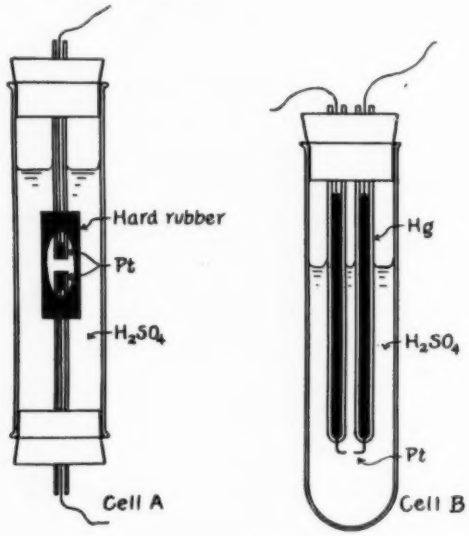


Fig. 3. Diagrams of electrolytic cells.

Results

Before giving the results of the capacity-frequency runs several of the precautions which were needed to secure consistent results will be described. The earliest experimenters found that the polarization capacity was a function of the applied voltage but that a constant value was approached as the polarization potential was reduced. This so-called initial capacity has the most significant theoretical explanation and is therefore of the most interest. Since this change of capacity with potential had only been determined for direct charge, however, it was thought worth while to make a few rough determinations of this relation at several frequencies. To measure the potential drop across the cell a transformer with an input impedance of about 15,000 ohms was shunted across, and a vacuum tube was attached to the out-

put as a detector. The change in plate current was read by means of a d.c. galvanometer. The whole transformer, vacuum tube, galvanometer system was calibrated throughout the frequency range and gave very satisfactory service, showing a change after a year's use which was less than the calibration errors. As all the curves giving the relation between capacity and potential were similar only one is shown in Fig. 4. The capacity C and phase angle ψ as defined above are both plotted against the potential drop at the electrodes, i.e., the total drop over the cell minus the drop due to the resistance of the electrolyte. The resistance of the cell was calculated from known conductivity data and from the dimensions of the cell. The most important points to be noted in these curves are the asymptotic values approached by

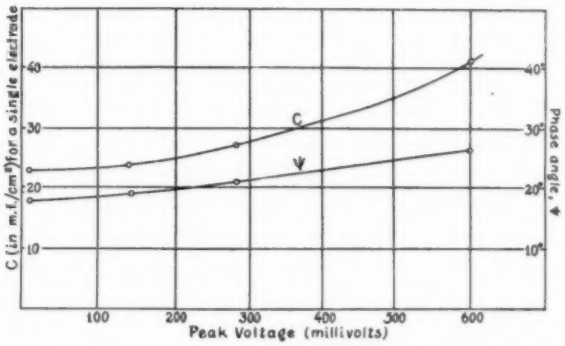


Fig. 4. Curve 1. Polarization capacity as a function of peak voltage at 1340 cycles per sec. Cell *A*, Pt−10% H_2SO_4.

the capacity and phase angle below .1 volt and their more rapid increase above this value. This limit for the initial capacity corresponds well with that found by direct charge methods.

In making the capacity-frequency measurements the potential applied to the cell was always kept below this critical value by determining the potential applied by means of the volt-meter, or, when this instrument could not be used, by reducing the current through the cell until further reduction caused no change in the bridge setting.

When the first measurements were made it was found that if it had taken some little time to make the reading with the comparison capacity, the cell did not immediately return to the same condition that it had previously shown. This was traced to a slight polarization which was set up in the cell when it was in the bridge circuit. Apparently even after the cell had been in the solution for a number of days some dissimilarities still existed in the electrodes which caused a small current to flow and polarize the cell. When the comparison

capacity was substituted for the cell the circuit was open and under the influence of diffusion and other causes this polarization gradually disappeared, to build up again when the cell was placed in the bridge circuit. It was thought best to eliminate this small variation by always measuring the capacity when the cell was self polarized. To do this connections were arranged always to keep the cell on short circuit while the comparison capacity was being used.

In making capacity tests it was at first thought that a very pure sine wave should be used in order to get reliable results because of the change of capacity with frequency. Now, although the vacuum tube oscillator gives a wave which is quite satisfactory for most alternating current bridge purposes it cannot be said to be entirely free from overtones. As no data were available on the effects of these overtones on the capacity measurements an investigation of their possible effect was made with some very interesting results. The method of procedure was as follows: Two oscillating circuits of different frequencies were simultaneously loosely coupled to the bridge input. The pitches were kept sufficiently different so that they could readily be distinguished and the bridge could be balanced with respect to either of them while the other was sounding. In this way capacity and resistance measurements were made with an alternating current of a certain frequency while one of any other desired frequency and intensity was at the same time present.

The results of this test showed conclusively that overtones were not affecting the measurements. The balance point determined by means of either pitch was absolutely independent of the presence or absence of the other. This was even true when the supposed disturbing pitch had an intensity greater than that of the pitch being used for measurement.

These facts have further application of interest. It has been suggested by various experimenters, laterly by Haworth[8] and Gunther-Schultze,[9] that the capacity in certain cells might be due to the formation of a thin gas film, or sometimes a poorly conducting layer varying from one to a few molecules in thickness, this film acting as the leaky dielectric of a thin parallel plate condenser. In order to explain on the basis of this theory the change of capacity with frequency, it is necessary to assume that the thickness of this film changes. Since it is the thickness of this film that determines the capacity and only one thickness is possible at any particular time, we must draw the conclusion

[8] Haworth, Far. Soc. Trans. 16, 365 (1920).
[9] Gunther-Schultze, Zeits. f. Physik 2, 36 (1920).

that when two frequencies are simultaneously impressed on the cell the capacity shall be the same for each. This is in contradiction with the observed facts. The theories of Warburg[5] and Kruger,[6] however, predict just the results that have been found true. The back electromotive force of polarization in their theories is determined by the solution of a partial linear differential equation of the second order in two variables, time and distance from the electrode, with one boundary condition determined by the form of the impressed current and the other by the fact that the function must vanish at ∞. Now it is known that if the function defining the first boundary condition be expressed as a sum of simple harmonic terms, the solution of such an equation will be of the same form, the coefficient of each term being independent of the other. Applying this to the experiment given above, the back electromotive force corresponding to each applied sine current will be independent of the presence of the other and therefore each pitch will keep its own capacity in agreement with the results of these experiments.

It is well known that the resistance of an electrolyte and also its polarization capacity have considerable temperature coefficients. To guard against the errors due to possible temperature changes while the measurements were in progress, the cells were in the later experiments constantly kept in ice filled Dewar flasks.

Another possible source of error enters when it is desired to make the measurements of capacity shortly after the electrodes have been immersed in the electrolyte. After a cell has been set up, its capacity changes quite rapidly for some time, so that it is necessary to make a correction for this effect. It was found that the rate of change of capacity was almost constant over a short time interval and that the proportionate change was nearly the same for the different frequencies. A true temperature coefficient of capacity could therefore be determined for some mean frequency, and the correction computed for each measurement when necessary.

With these precautions and corrections, very consistent results could be secured as will be shown by the succeeding curves. Curves 2, 3, and 4 (Fig. 5) show the results of some tests taken with Jolliffe's cell using sulphuric acid. A diagram of the electrodes of this cell is shown in Fig. 3 under the heading "Cell A." In these curves, there are plotted against frequency the polarization capacity C in Wien's formula and the phase angle ψ.

In order to make the interpretation of the results easier, logarithmic paper has been used. The slope at any point thus shows the power relation that holds at that point between the capacity and frequency.

The data plotted in curve 2 were taken before the radio frequency bridge had been set up, and while Jolliffe was still taking data. There is a gap, therefore, between 6000 and 120,000 cycles per second, but the change in the slopes of the capacity-frequency curves between these points is very apparent. The slope of the capacity curves plotted on logarithmic paper, although changing at the low frequencies, is very nearly .3; at high frequencies it is close to .5, as also determined by Jolliffe in other cases, who found at these frequencies that the

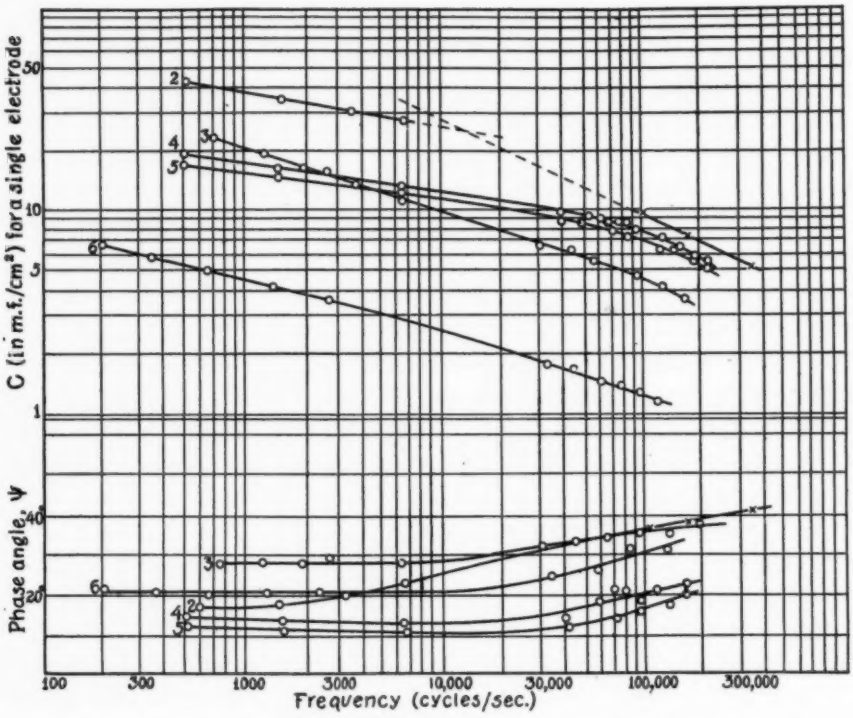


Fig. 5. Curves showing change in capacity with frequency. Curve 2, cell *A*, Pt−10% H_2SO_4; curve 3, cell *A*, Pt−1% H_2SO_4; curve 4, cell *A*, Pt −6% H_2SO_4; curve 5, cell *B*, Pt−6% H_2SO_4; curve 6, cell *A*, Au−1% H_2SO_4.

capacity was almost inversely porportional to the square root of the frequency. This curve also shows the increase in the phase angle which might have been expected from a comparison of the previous work in the low and high frequency ranges.

Curves 3 and 4 were taken with the same electrodes. The data for curve 3 were taken after the electrodes had been standing in the air for almost a year since last used. Before taking the data shown

in curve 4 the electrodes were remounted and polished and then left standing in distilled water until used. Both curves 3 and 4 are very similar to 2.

There was some doubt as to whether the change in the stream lines as the frequency became higher might not have been the cause of the change in the law at the higher frequencies. A cell with an entirely different arrangement of electrodes was therefore built to test this supposition. It is shown in Fig. 3 as "Cell B." The capacity-frequency relation for this cell is shown by curve 5. It will be noticed that it is very nearly of the same form as the others.

Curve 6 shows the same relations for a cell of the Jolliffe type using gold electrodes in sulphuric acid. It will be noted that although the capacity in this case happens to be approximately one quarter as great as in the case of platinum the curve form both for capacity and phase angle is substantially the same.

Conclusions

1. When two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell, the polarization capacity measured by means of either one is independent of the presence of the other.

2. The previous discordant observations giving change of capacity with frequency in a platinum sulphuric cell and gold sulphuric acid cell at low and high frequencies have been coordinated by showing that the law connecting capacity with frequency changes between 3000 and 100,000 cycles per second.

3. This change is due to a true polarization capacity effect and is not caused by change in stream lines in cell at high frequencies.

4. The initial capacity begins to change at the same potential for alternating current as it does for direct charge.

5. Confirming Jolliffe's[3] observations the Warburg and Kruger theories require modification in order to explain the change of phase angle and the increasing rate of change of capacity with frequency as the frequency is raised. These modifications in the theory will be discussed in an article to appear shortly.

In concluding the author wishes to express his appreciation to Professors C. C. Murdock and Ernest Merritt for their kindly help and genuine interest in the above work.

Physical Laboratory,
Cornell University,
Ithaca, New York,
January 27, 1926.

THE EMISSIVITY OF BISMUTH IN A MAGNETIC FIELD

By C. W. Heaps

Abstract

Electromagnetic theory and the experiments of Hagen and Rubens lead to the formula $\delta E/E=\delta\sigma/(2\sigma)$, where δE is the change produced in the emissivity E of a metal for long heat waves by a change $\delta\sigma$ in the electrical conductivity σ. Using a thermopile to detect δE a magnetic field of 4900 gauss was used to produce the $\delta\sigma$ in bismuth plates kept at about 100°C. No effect of the field on E was observed for polished surfaces, surfaces etched with nitric acid, or surfaces of a plate cast in vacuum. A change of E ten times smaller than the expected result could have been detected. Possible causes of the negative result are (1) the presence of emitted energy of too short a wave-length, (2) the absence of magneto-resistance in bismuth for high frequency currents, and (3) the absence of magnetoresistance in surface layers of bismuth. Reasons are given for rejecting (1) and (2) and accepting (3) as an explanation of the experiment.

THE behavior of a metal towards radiation of sufficiently long wave-length can be predicted in many respects from a knowledge of the conductivity of the metal. Maxwell's theory gives for the reflecting power, $R=100-200/\sqrt{\sigma T}$, where σ is the conductivity of the metal and T the period of the incident radiation. For waves longer than 4μ Hagen and Rubens[1] have verified this relation experimentally. If A is the absorbing power we have $A=100-R=200/\sqrt{T}$. By Kirchhoff's law we may write $A=E/e$, where E is the amount of radiation emitted per second by the metal and e is the amount emitted by a black body of the same area and temperature. Thus $E/e=200/\sqrt{\sigma T}$.

Any factor, therefore, which changes the electrical conductivity of a metal should change its emissivity for radiation of a particular period. It follows from the above equation that a small change, $\delta\sigma$, in the conductivity will produce a change δE in E, given by the equation $\delta E/E=-\delta\sigma/(2\sigma)$. A similar relation gives the change of absorbing power of the metal when its conductivity changes.

In 1898 Buisson[2] attempted to detect the change of absorbing power of bismuth when its resistance was increased by a magnetic field, but he failed to obtain positive results. His bismuth, in the form of thin electrolytically deposited plates, was transparent enough to allow visual observation of an illuminated window through the metal. A magnetic field capable of increasing the resistance of the plate by 60 percent failed to change the brightness of the observed image by any appreciable

[1] Hagen and Rubens, Ann. d. Physik **11**, 873 (1903).
[2] Buisson, Comptes Rendus **126**, 462 (1898).

amount. Buisson suggested as an explanation of his negative result that a magnetic field does not affect metallic resistance for the high frequencies of light waves. The more recent work of Hagen and Rubens has shown, however, that the equations given above, deduced by Maxwell's theory, do not apply for the high frequencies of visible light, but for waves in the infra-red, beyond 5μ, a very perfect agreement was obtained.[3] For these long waves the emissivity and reflecting powers of metals were found to vary in accordance with the theory when the conductivity was changed by altering the temperature of the metal. Constantan showed very little change of optical properties with temperature because its resistance changed very little.

It would appear probable, therefore, that Buisson's negative results were due to the employment of too short a wave-length. If the resistance change produced in bismuth by a magnetic field is similar in nature to the resistance change produced by a temperature elevation we should certainly expect an effect on the absorption and emission for radiation beyond 4μ.

The writer has performed experiments on bismuth using long waves and the expected effect has not been found.

Experiments

For several reasons it is more convenient to measure the energy emission of bismuth than its absorbing or reflecting power. The first experiment was performed on a bismuth plate, cast and polished. This plate, of dimensions $3\times5\times0.2$ cm approximately, was soldered to one side of a copper box and placed between the poles of a Weiss electromagnet. The pole-pieces were 3.5 cm apart and 10 cm in diameter. Water in the copper box was kept boiling by means of an electric heater, and a thermopile connected to a high sensitivity galvanometer was used to receive the radiated heat. The thermopile was mounted in a case provided with the usual shielded aperture and care was taken to exclude all radiation except that from the bismuth plate.

The galvanometer deflection was 27.0 cm and a magnetic field of 4900 gauss failed to produce any observable change in this deflection. The bismuth plate was then etched with nitric acid so that the crystal structure showed up very clearly, but the new surface gave no different result. There appeared, however, to be a thin film of impurity over the surface of the metal so a new plate was made as follows.

Bismuth was melted in a Pyrex bulb to which a second bulb with flat bottom had been sealed. The air was pumped out and the melted

[3] Wood, Physical Optics, p. 475. Hagen and Rubens found, however, an anomalous behavior in the case of bismuth.

bismuth agitated and heated for some time while the pump was running. By tilting the evacuated container the molten bismuth was now allowed to run into the flat-bottomed bulb where it solidified in the form of a plate. This plate was removed by breaking the bulb.

Both surfaces of the plate were apparently very clear and highly reflecting. By viewing these surfaces when illuminated by a single distant lamp, crystal faces could be observed flashing into view as the plate was rotated.[4] The average area of these separate crystal faces was probably about one square millimeter. This plate was clamped to one side of the copper box and the effect of the magnetic field on its emissivity determined. Neither face of the plate showed any change of emissivity capable of being observed.

The galvanometer deflection was 30.0 cm and a change as large as 0.2 cm could not have escaped detection. The value of $\delta E/E$ was thus less than 0.007. The value of $\delta\sigma/\sigma$ for bismuth spirals in the field used is about 0.15, and is probably of about this magnitude for the bismuth plates used. Thus the effect of the magnetic field on the emissivity must be at least ten times smaller than the effect to be expected from the conductivity change.

Discussion

To explain the absence of any effect of a magnetic field on the emissivity we may consider the possible operation of the following three factors.

1. The radiation may contain enough short waves to mask the effect of the field on the long wave emission. From the work of Hagen and Rubens we may assume that the emission of waves shorter than 4μ will be unaffected by the resistance change of the bismuth, while the emission of waves longer than 4μ is represented by the equations given above.

To get an estimate of the relative amounts of energy above and below 4μ we must know the form of the energy distribution curve. Aschkinass[5] has developed a theory for metals radiating waves longer than 4μ and has shown that Wien's displacement law becomes $\lambda_m\theta = 2660$, if θ is absolute temperature and λ_m is wave-length in microns. His theory also gives $S/E = 0.0221\,(r_0\theta/\lambda)^{\frac{1}{2}}$, where E is the ordinate of the energy distribution curve for a black body according to Planck's formula and S is the ordinate at the same temperature and wave-length of the energy distribution curve for the metal. r_0 is the resistivity of the metal at 0°C in ohm cms. It appears, therefore, that the

[4] This method of observing crystal structure is due to P. W. Bridgman, Proc. Amer. Acad. 60, 305 (1925).

[5] Aschkinass, Ann. d. Physik 17, 960 (1905).

energy distribution curve for the metal is of the same general shape as for a black body, but the maximum is displaced to shorter waves and the whole curve is relatively higher in the short wave region.

Wien's law, therefore, as modified by Aschkinass, gives $\lambda_m = 7.13\mu$ for the bismuth plate if its temperature is 100°C. Since the temperature must have been lower than this λ_m was somewhat greater than the above value. The theory of Aschkinass will not apply for radiation below 4μ. Rough graphical methods, however, may be applied to the curve for black body radiation, modified beyond 4μ in accordance with the theory of Aschkinass. Such methods make it appear very unlikely that more than one-twelfth of the energy radiated by the bismuth plate had a wave-length less than 4μ. This amount of energy, unaffected by the magnetic field, would not be sufficient to mask the effect of the field on the greater amount of energy in the long waves.

2. The resistance of bismuth for high frequency currents may not be changed by a magnetic field. It is known that the magnetoresistance of bismuth for alternating currents differs from that for direct currents. Heurlinger's theory,[6] however, which ascribes this difference to the interaction of galvano- and thermo-magnetic effects, appears to give a satisfactory explanation of the observed phenomena (which have been confined to lower frequencies than those of light). Heurlinger gives the equation $\rho' - \rho = -PQH^2$, where ρ' is the resistivity of the metal in the field H as the frequency of the current approaches infinity,[7] and ρ is the resistivity in the field for direct currents. P is the coefficient of the Ettingshausen effect and Q the coefficient of the Nernst effect. For bismuth in a field of 6000 gauss Heurlinger finds $-PQH^2/\rho_0 = 0.003$, where ρ_0 is the resistivity when $H = 0$. There is thus a difference of 0.3 percent between the a.c. and d.c. resistance of bismuth in a field of 6000 gauss when very high frequencies are used. The d.c. resistance change produced by this field is about 20 percent, so it appears that if Heurlinger's theory is complete, the high frequency magnetoresistance of bismuth differs very little from the d.c. magnetoresistance.

3. The surface layers of bismuth may be unaffected by the magnetic field while the body of the metal has its resistance changed. For several reasons[8] it appears probable that a magnetic field changes the resistance of bismuth by altering the number of electrons effective at any instant in carrying the current. If equilibrium exists between a group of conducting electrons and a group of bound electrons it is entirely conceivable that a magnetic field may alter the equilibrium

[6] Heurlinger, Phys. Zeits. **17**, 221 (1916).

[7] Resistance change due to skin effect is not considered in the theory.

conditions so as to change the number of electrons in the respective groups. The molecules on the surface of the metal will be subjected, because of surface tension effects, to conditions different from those in the body of the metal. These molecules may react differently, therefore, towards a magnetic field.

There is considerable evidence in favor of this view. Magnetoresistance for thin bismuth films is smaller than for bismuth in bulk; and the thinner the film the less appears to be the magnetoresistance. Films which have been examined in this respect by Curtiss[9] consisted of small crystals of random orientation. If the crystal composition of the films of different thicknesses (as determined by resistance measurements) was the same the magnetoresistance differences must have been due to the increased relative importance of surface layers for the thinner films. There is some doubt, however, of the identity of crystal structure of the different films.

It seems to be certain that the position relationship of molecules of a metal to each other is of profound influence on the magnetic quality of the metal. Thin amorphous films of nickel are non-magnetic.[10] Liquid metals do not show a true magnetoresistance. Surface layers of iron appear to have a smaller induction than deeper layers, while the converse is true for nickel.[11]

Conclusion

While the experimental evidence is not conclusive it nevertheless seems probable that the failure of a magnetic field to affect the emissivity of bismuth is due to the absence of magnetoresistance in the surface layers of the metal. Hagen and Rubens found bismuth occupying an anomalous position as regards reflection and emission coefficients in the list of metals which they investigated. They suggested as reasons for this peculiarity the difficulty of securing good reflecting surfaces of bismuth and the known anomalous behavior of bismuth in other respects. It is possible that the electrical resistance of surface layers of bismuth is different from the body resistance even when no magnetic field acts.

The Rice Institute,
Houston, Texas,
March 20, 1926.

[8] Heaps, Phys. Rev. **19**, 7 (1922); **12**, 340 (1918); Phil. Mag. **50**, 1001 (1925).

[9] Curtiss, Phys. Rev. **18**, 255 (1921).

[10] Ingersoll and DeVinney, Phys. Rev. **26**, 86 (1925).

[11] McKeehan, J.O.S.A. and R.S.I. **11**, 169 (1925), has attributed this effect to strains in the surface layers produced by previous treatment, but on this view it is difficult to explain some of the results of E. H. Williams, Phys. Rev. **33**, 60 (1911).

TEST FOR SPACE QUANTIZATION IN A MAGNETIC FIELD

By B. B. Weatherby and A. Wolf

Abstract

The heterodyne beat method was used to detect a possible change in the dielectric constant of gases, due to space quantization in a magnetic field. A condenser, forming a part of one oscillating circuit of about 1,000,000 cycles frequency, was filled with the gas investigated and the magnetic field then applied. The results obtained show that for helium (20 cm pressure), air (76 cm) and oxygen (76 cm) at room temperature there is no change in the dielectric constant to 1 part in 500,000. The magnetic field was of the order of 7000–8000 gausses, while the electric field was estimated at 5000–10,000 volts/cm. The tests were carried out with the direction of the electric field both parallel and normal to the direction of the magnetic field.

IN a recent article,[1] Ruark and Breit suggested that it might be possible to test for space quantization of gases in a magnetic field through a comparative determination of the dielectric constant of the gas across and along the lines of force of the magnetic field. If we consider an atom to be an electrical doublet subjected to space quantization in a magnetic field, it is reasonable, even in the absence of any accurate calculation, to expect an appreciable change in the dielectric constant of the gas when the field is applied. The magnitude of this change ought moreover to be different, depending on whether the electric field, used for the determination of the dielectric constant, is parallel to the magnetic lines of force or perpendicular to them. Since the changes in dielectric constant so produced may be very small, a highly sensitive test must be used in looking for them.

So little is known with regard to the interaction of electric and magnetic fields in the atom that negative results of experiments along these lines need not necessarily be considered an evidence against space quantization. It is thought that such studies are nevertheless of interest in connection with theories of atomic structure.

The test for a possible change in the dielectric constants of oxygen, air, and helium, in a magnetic field, was carried out by means of apparatus essentially the same as a Whiddington ultramicrometer,[2] consisting of two modified Hartley oscillators. The condenser in one of these was variable and used for the adjustment of the beat frequency. The condenser in the second circuit was made of two aluminum plates 2×10 cm separated by about 0.2 mm and was fixed in

[1] Ruark and Breit, Phil. Mag. 49, 504 (1925).
[2] Whiddington, Phil. Mag. 40, 634 (1920).

value. This second condenser was enclosed in a glass tube filled with the gas investigated and placed between the poles of a Du Bois electromagnet. The usual precautions, with regard to shielding, were observed.

Details of the circuit arrangement are shown in Fig. 1. Western Electric 5-watt tubes were used as oscillation generators. The system of chokes and blocking condensers was necessary in order to make possible the use of a single high tension battery.

The oscillation frequency was about 1,000,000 cycles per second and the beats were sufficiently steady over short intervals of time to permit the making of measurements. A residual drift and variation

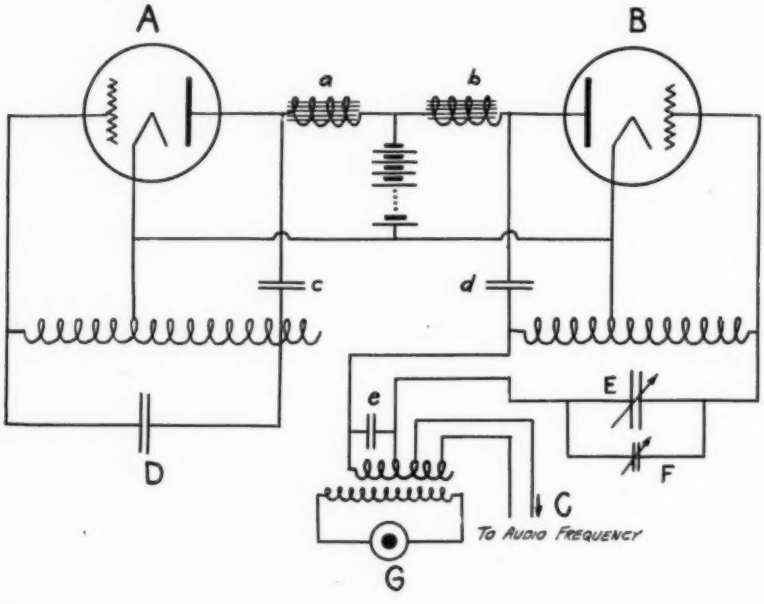


Fig. 1. *A*, *B*, vacuum tubes; *D*, fixed condenser; *E*, *F*, variable condenser and vernier; *G*, loud speaker; *a*, *b*, *c*, *d*, *e*, choke coils and radio frequency by-pass condensers.

observed in the beats was believed to be due to three causes; (1) charges collecting on the inner walls of the vacuum tubes, (2) motion of the shielding plates due to humidity and temperature changes in the room, (3) imperfect insulation.

The usual procedure was as follows: the variable condenser was adjusted until the beats could be easily counted; the number of beats in a given time was taken with the magnetic field off; the current in the electromagnet was then switched on and the number of beats in the same interval of time counted again. This was done first with the condenser plates set parallel and then with them perpendicular to the magnetic field.

A few typical readings are given below.

	Number of beats in 2 sec.								
	oxygen			helium		air	(brass case condenser)	
Magnetic field off:	8	8	6	6	6	12	12	
Magnetic field on:	8	7	6	7	8	12		

Each of these sets of observations was taken with a fixed setting of the variable condenser.

When using the condenser described above there was almost always observed a small change in the beat frequency when the current in the magnet was turned on. This change however corresponded to a variation of the frequency of the oscillating circuit of less than one part in a million. The same change was observed when the glass tube containing the fixed condenser was evacuated and it was therefore ascribed to a mechanical effect of the magnetic field on the condenser. A condenser of different design with plates clamped rigidly inside a metal case eliminated the effect completely. This second condenser was, however, used only in the experiments with air.

The observations show that with an electric field estimated at 5,000–10,000 volts per cm the oscillation frequency did not change by more than 1 part in a million when a magnetic field of 7000–8000 gausses was applied. Air and oxygen were investigated at atmospheric pressure and helium at a pressure of 20 cm Hg. All observations were made at room temperature.

As the formula for the frequency of an oscillating circuit is $f = 1/2\pi\sqrt{LC}$ the above results mean that the dielectric constants of the gases investigated do not change by more than 1 part in 500,000 when a magnetic field is applied under the conditions of the experiment. (No correction was here applied for the capacity of the leads.) Different results might have conceivably been obtained at low temperatures or with a smaller electric field.

The dielectric constants of gases at ordinary pressures are so close to unity that a precision of 1:500,000 in the dielectric constant corresponds to much less precision when the average polarization of the atoms and molecules is considered. Under the conditions of the experiment our results show that when the magnetic field is applied, the average electrical polarization of oxygen and air does not change by more than 1:250 of its value, while that of helium, which was used at a lower pressure and has a dielectric constant closer to unity, does not change by 1:10 of its value.

In conclusion we wish to express out thanks to Professor C. B. Bazzoni who suggested carrying out this test.

RESEARCH SECTION, RANDAL MORGAN PHYSICS LABORATORY,
UNIVERSITY OF PENNSYLVANIA,
January 1926.

THE HALL EFFECT IN BISMUTH WITH LOW MAGNETIC FIELDS

By Palmer H. Craig

Abstract

The Hall effect in bismuth for a magnetic field strength of from 0.07 to 1.00 gauss was accurately determined by improved methods. *Production of the bismuth films.* Various methods for obtaining excessively thin, homogeneous bismuth films were tried and compared, such as casting, electroplating, evaporating, sputtering, and metallic spraying, of which the last three methods were particularly successful. *Measurement of very low voltages.* By refinements made in the potentiometer and measuring circuits, readings to one-tenth microvolt were accurate and reproducible. *Magnitude of the Hall effect at low fields.* The value of the Hall coefficient, R, is abnormally large between 0.07 and 0.30 gauss, having a value of -171 at 0.07 gauss, as compared with a value of -11 which R had for this film at 15 gausses. The value at 4220 gausses was -29. A curve is plotted showing the rapid decrease in the value of $-R$ between 0.07 and 0.30 gauss, and comparison is made with the higher values of field strength. It is noted that by putting the Hall potential of one film in series with one or more other films we obtain comparatively high values of the Hall e.m.f. which may be applied to great advantage as an alternating current rectifier in radio and similar applications.

Introduction

SINCE the discovery of the Hall effect in 1875 much has been done to elucidate this phenomenon both experimentally and theoretically. But, with the exception of Righi,[1] who employed fields comparable to that of the earth, and a few others, almost all investigators have used strong fields. It is important to know accurately the effect of low fields, to compare it with the known facts and to determine whether any abnormal relations exist. As the effect of the magnetic field is small in all cases, a great refinement in the potentiometer and measuring circuits is imperative with weak fields, and the preparation of the bismuth strips presents great difficulties and requires special methods.

Preparation—Experimental Arrangements

Since the Hall effect increases with the thinness of the metallic strip, the first requisite was to prepare extremely thin films of metal. Bismuth and tellurium, which have the highest Hall coefficient of the ordinary metals, were selected and six different methods were tried in order to find the best and quickest way of making films which

[1] Righi, Jour. d. Physique 3, 127 (1884).

would be extremely thin and at the same time electrically continuous. These processes were casting, dipping, spraying, electroplating, evaporating, and sputtering.

Thin films of bismuth cannot be produced by casting unless pressure is exerted on the surface of the metal as it cools, and provision must then be made for lateral expansion when solidifying.

Surprisingly thin and uniform films were, however, obtained by dipping mica sheets into molten bismuth and using the metallic film which adhered to the mica. If the surface of the mica be slightly roughened with hydrofluoric acid, and care be used in withdrawing the mica from the molten metal, a very thin and uniform film can be obtained by this very simple and rapid method.

Much work was done by the author to produce very thin plates of bismuth and tellurium by the process of spraying molten metal. Excellent results were obtained both with the "Schoop" compressed air metallic spraying process, and also with the "Gravitas" metal dust spraying process. Cooperation in this part of the work was kindly rendered by the Metals Coating Company of Philadelphia. Both of these spraying processes involve spraying metals in the molten state by means of a compressed air gun. In the case of bismuth it was found advisable to use compressed nitrogen, instead of air, in order to prevent oxidation of the sprayed layer. When applied to mica, glass, and bakelite, excellent films of both bismuth and tellurium were obtained.

Attempts to produce homogeneous films by electroplating met with poor results, even when great care was used as regards temperature, speed of the rotating cathode, and concentration of solution.

Evaporation of molten bismuth in a partial vacuum produced very good results. Bismuth was placed inside an evacuated bell-jar and was melted by an electric heater. A glass plate, suspended above the arrangement, collected the evaporated bismuth in the form of excellent films.

Cathodic sputtering undoubtedly produces the thinnest films of any method. With reasonable care bismuth films can easily be prepared by this method so thin as to be quite transparent. Sputtering was accomplished by applying the secondary current of a 20,000 volt transformer to anode and cathode electrodes placed inside a bell jar evacuated to 30 microns. Rectification of the secondary current by a kenetron accelerated the action. A disc of bismuth 3.5 inches in diameter was used as a cathode, and the glass plate on which the film was to be sputtered was placed just outside the Crookes' dark space,

which was about 2 cms long. With a current of 5 milli-amperes excellent films were produced on glass in about 20 minutes.

Disposition of the Apparatus

The very weak magnetic fields employed in this work were obtained from an air core solenoid. When a given current is passed through such a coil the field at the center is easily calculated. This calculated value was checked by a calibrated ballistic galvanometer in conjunction with a flip coil. The actual coil employed consisted of 100 turns of wire wound on a rectangular wooden form 8×11 cm in cross-sectional area, the size of this form being just large enough to accommodate the film used. The inductance of this coil was 2.5 millihenries, and it was therefore necessary to pass 35.2 milli-amperes through it in order to get a field of one gauss at the center. Because of the extremely low values of magnetic field used, it was necessary to shield the arrangement carefully from any action of the earth's and stray fields. Several methods were tried to accomplish this shielding, the one finally adopted being that of placing the set-up so that the plane of the bismuth film coincided exactly with the magnetic inclination of the earth's field at that point, thus eliminating any magnetic component in a direction perpendicular to the plane of the metallic film. Care was taken to keep all iron away from the vicinity of the apparatus, and upon actual measurement stray fields were found to be negligible.

Chemically pure bismuth for producing the films was furnished by Eimer and Amend and the film itself, obtained by any one of the previously described methods, was mounted on bakelite with sodium silicate as a binder. Contact at the ends for the longitudinal current was made by phosphor-bronze spring clips, and contact at the edges of the film, for picking up the transverse Hall potential, was obtained by means of small brass fingers attached to machine screws passed through the bakelite. The surface of the film was carefully cleaned with weak hydrochloric acid solution to remove surface oxides, and the entire film and connections were then painted with sodium silicate to keep semi-conducting layers of dirt and moisture from collecting on the surface of the film. In some cases it was even found advisable to mould the entire arrangement in sulphur to obviate this difficulty.

Since the potential differences to be measured were of the order of one microvolt, extreme care was taken to render the measuring apparatus very accurate and stable. The transverse Hall effect potential was measured by means of a Leeds and Northrup type K potentiom-

eter, redesigned with a system of calibrated external shunts which increased the sensitivity of the instrument ten times. Four galvanometers of varying degrees of sensitivity were used with potentiometer for null readings, the most sensitive galvanometer having a sensitivity of 12.2 mm per M.V. The longitudinal current through the film was supplied by large storage cells, the output of which passed through a large filter system of two very large inductances in series with the line, the lines being shunted by two condensers of six microfarads each. This filter eliminated erratic action caused by sudden fluctuations of the longitudinal current occasioned by bubbling of the cells.

The main current through the potentiometer itself was passed through a similar filter and was allowed to flow over night before taking readings so that greater stability could be expected. The null potentiometer reading on the standard cell was checked before and after each measurement.

Great care was taken to eliminate all spurious effects. Thermal effects, of course, constituted the greater part of these corrections. Junctions of dissimilar metals in the circuit were reduced to a minimum, and the remaining potentials due to Thomson and allied effects were accurately measured the instant the longitudinal current was broken. Grounding one side of the potentiometer circuit was found to increase stability.

For the work at high magnetic fields, a large electromagnet was used. This magnet was capable of producing a field of 18,000 gausses in a narrow air gap, the field of which was measured by a calibrated ballistic galvanometer in conjunction with a flip coil.

Experimental Results and Discussion

Using a bismuth film obtained by metallic spraying, 3.5×8.0 cm in area and 0.012 cm thick, the results shown in Table I were obtained. These results are in agreement with those obtained with films of the other types described previously. In this table three different ranges of magnetic field strength were investigated with the same bismuth film and under the same general conditions. A longitudinal current of 1.5 amperes was used throughout Table I. The "residual" e.m.f. (measured in microvolts) which is referred to in the second column is the potential difference caused by the fact that the brass fingers which pick up the transverse Hall potential cannot possibly be placed at exactly equipotential spots with regard to the longitudinal current. These contacts were placed as near to equipotential points as possible and the remaining difference of potential was measured as given in

the second column of the table. The second and third columns automatically include the sum of the thermal effects, since it is of course impossible to eliminate these thermal potentials from the potentials indicated in these columns. However, the spurious effects are eliminated when column two is subtracted from column three in order to get the net Hall e.m.f. in the fourth column. The Hall coefficient, R, given in the fifth column is calculated from the usual formula,[2] $R=Ed/IH$, where R is the Hall coefficient, d the thickness of the film in centimeters, I the longitudinal current in abamperes, H the magnetic field strength in gausses, and E the net Hall e.m.f.

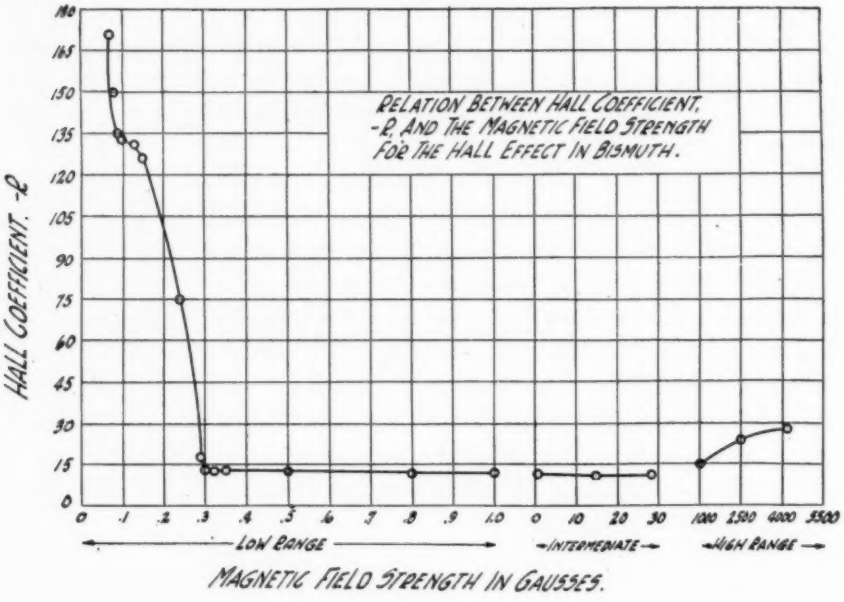


Fig. 1

It is immediately apparent that the Hall coefficient is abnormally high in the range of very low fields, and falls rapidly in value as the field is slightly increased. Reference to the graph shows a slight irregularity near 0.1 gauss, a straightening out of the curve at about 0.3 gauss, and then an approximately linear relation until a field strength of 1.0 gauss is reached. Readings in an intermediate range of zero to 30 gausses showed that $-R$ is practically constant at a value of 11 throughout this range. This value agrees very well with the value of 10.27 which Von Ettingshausen and Nernst[3] found for bismuth at a field of 1650 gausses. In the range from 1000 to 4200 gausses the

[2] L. L. Campbell, "Galvanomagnetic and Thermomagnetic Effects," p. 9.

coefficient increases slightly from 15 to 29. This curve was selected from a dozen similar graphs as being one of the most representative, and the irregularity in the neighborhood of 0.1 gauss is typical of similar irregularities in all curves obtained with the various films.

These results show that the value of $-R$ at very low fields is higher than has been heretofore suspected and that the curve for $-R$, plotted against field strength, shows a marked rise in this low range.

Each of the values in Table I are average values for approximately twelve readings at each value of field strength. These readings are reproducible to approximately one-tenth of a microvolt, and the readings forming the averages did not vary more than this amount.

During the course of the experiments an interesting incidental fact was discovered, namely that the Hall potential of one film may be put in series with that of one or more other films, the sum of these series potentials agreeing very well with the calculated sum of the Hall potentials of the individual films as observed separately. Al-

TABLE I

Hall effect in bismuth for low, intermediate, and high fields

Field strength (gausses)	"Residual" e.m.f. (μ volts)	"Residual" + Hall e.m.f. (μ volts)	Net Hall e.m.f. (μ volts)	-R
.07	14.0	15.5	1.5	171
.08	14.1	15.6	1.5	150
.09	14.2	15.7	1.5	135
.10	14.2	15.8	1.6	133
.13	14.4	16.1	1.7	131
.15	14.3	16.9	2.6	126
.24	14.0	16.3	2.3	75
.29	14.6	21.1	6.5	18
.30	14.5	19.8	5.3	14
.32	14.4	19.6	5.2	13
.35	14.8	20.5	5.7	13
.50	14.6	22.7	8.1	13
.80	14.6	26.6	12.0	12
1.00	14.6	29.6	15.0	12
1.0	14.5	29.5	15.0	12
15.0	14.3	35.1	20.8	11
28.5	14.4	60.4	46.0	11
1000	14.0	1889.0	1875.0	15
2500	14.0	7514.0	7500.0	24
4220	14.0	15324.0	15310.0	29

though this fact has little application where quantitative readings of a high degree of accuracy are desired, it is of real importance in any application where larger values of Hall potential are desirable than those which can be obtained with a single film. The author is at

[3] Von Ettingshausen and Nernst, Wied. Ann. 29, 343 (1886).

present using this additive principle in an application of the Hall effect to rectification of alternating current with a method similar to that described by DesCoudres.[4] The additive principle used in this connection produces a Hall potential of several volts in low fields with thin bismuth films, and thus gives the Hall effect a practical importance as a rectifier, especially in radio and similar applications. Work on the additive principle is also being done by Sarek.[5]

The results here presented indicate that there is considerable work to be done in further investigating abnormalities in the Hall coefficient at very low fields, and also suggest that certain modifications or explanations will have to be introduced into the theory of the Hall effect to account for the interesting changes in the Hall coefficient at low fields.

In conclusion, the author wishes to acknowledge his indebtedness to Dr. Louis T. More, Dr. R. C. Gowdy, and Dr. S. J. M. Allen for their kind help and valuable advice tendered throughout the progress of the work.

UNIVERSITY OF CINCINNATI,
PHYSICS LABORATORY,
August 2, 1925.

[4] Des Coudres, Phys. Zeits 2, 586 (1901).
[5] Sarek, Eleck. u. Maschinenbau, 43, 172 (1925).

THE RATIO OF HEAT LOSSES BY CONDUCTION AND BY EVAPORATION FROM ANY WATER SURFACE

By I. S. Bowen

Abstract

It is shown that the process of evaporation and diffusion of water vapor from any water surface into the body of air above it is exactly similar to that of the conduction or "diffusion" of specific heat energy from the water surface into the same body of air. Because of this similarity it is possible to represent the ratio R of the heat loss by conduction to that by evaporation by the formula

$$R=.46\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760}$$

where T_a and P_a are the original temperature and vapor pressure of the air passing over the lake, and T_w and P_w are the corresponding quantities for the layer of air in contact with the water surface. The substitution of R times the evaporation loss for the value of the conduction heat loss in the Cummings equation for evaporation makes it an exact equation for the determination of evaporation from any water surface in terms of the net radiant energy absorbed by the water and the heat stored in the water.

IN his study of evaporation from lakes, Cummings[1] has assumed, as a first approximation, that the determining factor is the incoming solar radiation, i. e. that the evaporation from any lake is roughly equal to the radiant energy falling on the lake divided by the latent heat of vaporization, corrected, of course, for heat stored in the lake due to any change in its temperature. This would be strictly true if we could neglect other heat losses such as conduction and convection, for since evaporation increases rapidly with the temperature, the lake would warm up to such a temperature that the heat lost by evaporation would be just equal to that gained by solar radiation. Wind and humidity would then not affect the total evaporation, but only the temperature that must be reached before equilibrium between evaporation and solar radiation is attained. The present paper is a theoretical attempt to evaluate losses by conduction and convection in terms of easily measurable quantities, and hence to determine whether they are small enough to be neglected; and if not, how they may be corrected.

In order to simplify calculations, we shall assume in the first part of the paper that diffusion coefficients, conductivities, and densities are independent of the temperature. We can write at once for the

[1] Cummings, Phys. Rev. 25, 721 (1925); Journal of Electricity 46, 491.

mass m, of water vapor diffusing per unit time across a space of length l, and area a,

$$m = D_1 a(\rho_1 - \rho_2)/l \tag{1}$$

ρ_1 and ρ_2 are the densities of water vapor on the two faces of the space and D_1 is the diffusion coefficient of water vapor through air.

If we multiply both sides of this equation by L, the latent heat of vaporization, we get

$$Lm = D_1 a(L\rho_1 - L\rho_2)/l \tag{2}$$

and if let θ_1 and θ_2 represent the energy per unit volume in the form of latent heat, the energy Q_L carried across becomes

$$Q_L = D_1 a(\theta_1 - \theta_2)/l \tag{3}$$

Likewise we can write the formula for the heat energy Q_S carried, by conduction, across the same space as above:

$$Q_s = Ca(T_1 - T_2)/l \tag{4}$$

where C is the conductivity of the air in the space and T_1 and T_2 are the temperatures of the two faces.

If we substitute $C = D_2 C_p d$, where D_2 is the "diffusion coefficient" or diffusivity for the heat energy, C_p is the specific heat at constant pressure, and d is the density of the air, (4) becomes

$$Q_s = D_2 a(T_1 C_p d - T_2 C_p d)/l \tag{5}$$

Or if we let φ_1 and φ_2 be the densities of specific heat energy at the two faces,

$$Q_s = D_2 a(\varphi_1 - \varphi_2)/l \tag{6}$$

It is seen at once that (3) and (6) are of exactly the same form, the only difference being in the values of D_1 and D_2, which, in fact, differ only by a few percent, (a relationship predicted by the kinetic theory). This leads one to expect that heat losses by evaporation and diffusion, and by conduction, will follow the same laws and will be affected in the same way by convection.

Consider the case of a lake over which a wind is blowing (Fig. 1). Let y be the distance from the windward side of the lake measured parallel to the direction of the wind. Assume that the velocity of the wind at a distance x above the surface of the lake is $f(x)$ and also that this velocity is large enough so that the velocity of horizontal diffusion is negligible in comparison with it. Then for any element of volume $dxdydz$ the amount of latent heat entering the volume per unit time

from the lower side is $-D_1(\partial\theta/\partial x)\,dy\,dz$, while on the upper side the amount leaving is

$$-\left[D_1\frac{\partial\theta}{\partial x}+\frac{\partial}{\partial x}\left(D_1\frac{\partial\theta}{\partial x}\right)dx\right]dydz\,.$$

The difference, if we assume D_1 constant, is then $D_1(\partial^2\theta/\partial x^2)dxdydz$. When a steady state is reached this net gain must be carried away by the air passing through the volume in unit time. The air in passing

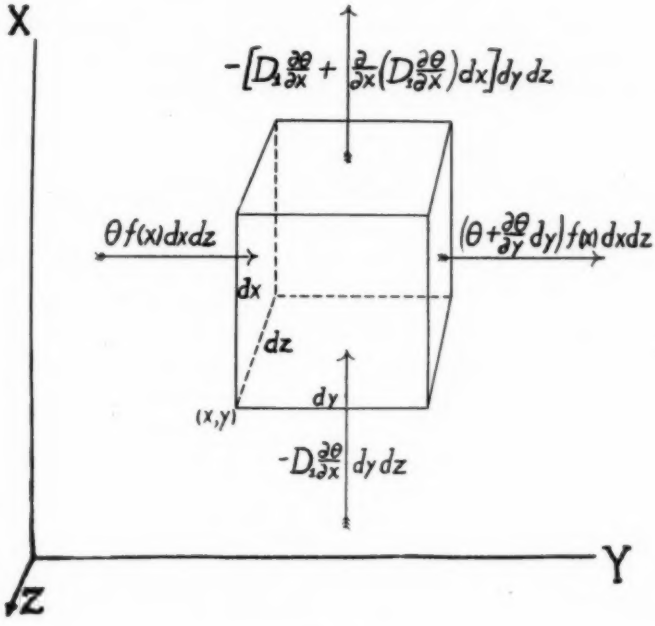


Fig. 1.

through the volume $dxdydz$ has its density of latent heat changed from θ to $\theta+(\partial\theta/\partial y)\,dy$; and since the volume passing per unit time is $f(x)dxdz$ the total amount carried away is $(\partial\theta/\partial y)\,f(x)dxdydz$.

Equating these two quantities we get

$$\frac{\partial\theta}{\partial y}f(x)=D_1\frac{\partial^2\theta}{\partial x^2} \tag{7}$$

and by similar reasoning,

$$\frac{\partial\varphi}{\partial y}f(x)=D_2\frac{\partial^2\varphi}{\partial x^2} \tag{8}$$

as the general equations determining θ and φ at all points above such a lake. The boundary conditions are $\varphi=\varphi_1$, $\theta=\theta_1$ at $x=0$, and $\varphi=\varphi_2$,

$\theta=\theta_2$ at $y=0$. φ_2 and θ_2 represent the energy density, in the form of specific and latent heat respectively, of the incoming air, and φ_1 and θ_1 represent the corresponding densities for the layer of air in contact with the water.

Since it is impossible to obtain a general solution of these equations for any function $f(x)$ we will consider certain special values of $f(x)$.

Case I. $f(x)=K$ from $x=0$ to $x=a$ and $f(x)=0$ from $x=a$ to $x=\infty$. If a and K are small and the lake large, then the layer of air from $x=0$ to $x=a$ will have its temperature changed to that of the water and will become saturated with water vapor, i. e., its specific heat density will change from φ_2 to φ_1 and its latent heat density from θ_2 to θ_1. Evidently the ratio R of heat lost by conduction to that lost by evaporation is

$$R=(\varphi_1-\varphi_2)/(\theta_1-\theta_2) \tag{9}$$

since this is the ratio of the two kinds of energy taken on by each cubic centimeter of the air passing over the lake.

Case II. $f(x)=0$, from $x=0$ to $x=a$; $f(x)=K$, from $x=a$ to $x=\infty$. If the area of the lake is small and the velocity K large, then the water vapor and heat diffusing through the stationary layer from $x=0$ to $x=a$, will be carried away immediately and we can assume $\varphi=\varphi_2$, $\theta=\theta_2$ at the layer $x=a$. Under these conditions the rates at which heat and water vapor leave the water surface are determined solely by diffusion and the ratio between them is simply equation (6) divided by (3).

$$R=D_2(\varphi_1-\varphi_2)/D_1(\theta_1-\theta_2) \tag{10}$$

Case III. $f(x)=Kx^n$ from $x=0$ to $x=\infty$. Professor Epstein has obtained equation (11) as a solution for this value of $f(x)$.

$$\theta=\theta_1+(\theta_2-\theta_1)\frac{\displaystyle\int_0^{x\left[\frac{K}{(n+2)^2D_1y}\right]^{\frac{1}{n+2}}} e^{-\sigma^{n+2}}d\sigma}{\displaystyle\int_0^{\infty} e^{-\sigma^{n+2}}d\sigma} \tag{11}$$

But the rate of diffusion from unit area of the water surface, i. e., diffusion across the plane $x=0$, is

$$Q_L=-D_1\left(\frac{\partial\theta}{\partial x}\right)_{x=0}=\frac{D_1(\theta_1-\theta_2)\left[\frac{K}{(n+2)^2D_1y}\right]^{\frac{1}{n+2}}}{N} \tag{12}$$

where

$$N = \int_0^\infty e^{-\sigma^{n+2}} d\sigma$$

Similarly

$$Q_e = -D_2\left(\frac{\partial \varphi}{\partial x}\right)_{x=0} = \frac{D_2(\varphi_1-\varphi_2)\left(\dfrac{K}{(n+2)^2 D_2 y}\right)^{\frac{1}{n+2}}}{N} \tag{13}$$

which gives at once

$$R = \frac{Q_e}{Q_L} = \left(\frac{D_2}{D_1}\right)^{\frac{n+1}{n+2}} \left(\frac{\varphi_1-\varphi_2}{\theta_1-\theta_2}\right) \tag{14}$$

This ratio is independent of y and therefore holds for every square centimeter of the lake and also for the lake as a whole.

Discussion

Case I represents a condition where the whole quantity of air under consideration is completely changed in temperature and moisture content to that of the layer of air in contact with the water. For this reason diffusion is not the limiting factor and hence the diffusion coefficients do not enter into the formula for the ratio of the heats lost by the two processes. It is obvious, however, that if conditions are such that diffusion does enter, it will be in such a way as to increase the loss by the process having the larger diffusion coefficient relative to the loss by the other method. Hence under any conditions of wind we may say, since $D_1 > D_2$ that

$$R \leq (\varphi_1-\varphi_2)/(\theta_1-\theta_2) \tag{15}$$

Case II, on the other hand, represents conditions where diffusion is the completely determining factor, the heat and water vapor being immediately carried away after diffusing through the stationary layer. If, however, these are not immediately carried away, they tend to build up the temperature and vapor density on the upper side of this layer, and thus decrease the gradient in the stationary layer. This in turn tends to slow down further diffusion. But the process with the larger diffusion coefficient will build up faster, and hence will be retarded more than the one with the lower diffusion coefficient. Hence we can write

$$R \geq D_2(\varphi_1-\varphi_2)/D_1(\theta_1-\theta_2) \tag{16}$$

The results of Case III support these conclusions since for all values of $n \geq 0$.

$$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}} \left(\frac{\varphi_1-\varphi_2}{\theta_1-\theta_2}\right) \geq R \geq \frac{D_2}{D_1}\left(\frac{\varphi_1-\varphi_2}{\theta_1-\theta_2}\right) \tag{17}$$

Negative values of n are without physical meaning since they would involve an infinite velocity at $x=0$. The upper limit of R in (17) corresponds to the case $f(x)=K$, *i. e.*, a wind of uniform velocity. The values between this limit and the limit set by Case I correspond to conditions where $f(x)$ is a decreasing function of x, and hence do not correspond to actual conditions over a lake.

The above discussion shows that R lies under all conditions between the values given by Case I and Case II. For these two very simple cases, however, it is no longer necessary to assume D, C, and ρ independent of the temperature.

Thus in Case I, if we consider the changes in an amount of gas that would occupy 1 cc at 0°C, the amount of heat necessary to warm it from the temperature of the air, T_a, to the temperature of the water, T_w, is

$$Q_s = d_0 C_p \frac{P}{760}(T_w - T_a) \tag{18}$$

where d_0 is the density of air at 0°C, 76 cm, C_p is the specific heat at constant pressure, and P is the pressure of the air in mm. Likewise the amount of heat taken on in the form of latent heat when this amount of air is brought to saturation at the temperature T_w is

$$Q_L = L\left(\frac{\rho_w T_w - \rho_a T_a}{273}\right) \tag{19}$$

where as before ρ_a and ρ_w are the densities of water vapor in the incoming air and in the layer of air in contact with the water respectively. Therefore

$$R = \frac{Q_s}{Q_L} = \frac{d_0 C_p \frac{P}{760}(T_w - T_a)}{L\left(\frac{\rho_w T_w - \rho_a T_a}{273}\right)} \tag{20}$$

Similar consideration, which take into account the known temperature coefficients of heat conduction and diffusion, give for Case II

$$R = \frac{C_0 (T/273)^{\gamma_1}(T_w - T_a)}{L D_{1,0}(T/273)^{\gamma_2}(\rho_w T_w - \rho_a T_a)760/P} \tag{21}$$

where C_0 and $D_{1,0}$ are the value of the conductivity and diffusion coefficient at 0°C. Kinetic theory gives $\gamma_1=\gamma_2=\frac{1}{2}$, while experimental data indicate a somewhat larger value, but still make $\gamma_1=\gamma_2$.

If we substitute in these formulas the following experimental data: $d_0=.001293$, $D_0=.206$, $C_0=.0000566$, $C_p=.241$, $L=585.$, $\rho_a T_a/273=P_a/9.41\times10^5$, $\rho_w T_w/273=P_w/9.41\times10^5$, where P_a and P_w are the corresponding partial pressures of water vapor expressed in mm of mercury, we get

Case I.

$$R=.501\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760} \tag{22}$$

Case II.

$$R=.442\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760} \tag{23}$$

Case III, however, shows that under ordinary conditions where $f(x)$ is an increasing function of x, the true R is nearer Case *II* than Case *I*. Hence we may take as the most probable equation

$$R=.46\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760} \tag{24}$$[2]

This equation is, of course, valid only for value of T_w low enough that the volume of the air is not appreciably increased by the water vapor evaporating into it and also that the water vapor on diffusing into the cooler air above does not condense and fall back to the water surface. This last condition is only violated under certain extreme conditions since the air is being warmed by conduction nearly as fast as its dew point is being raised by the diffusion of water vapor into it.

As an example let $T_w=20$°C, $T_a=15$°C, Relative humidity $=.5$, $P=760$ mm. This gives $R=.21$ which indicates that while the ratio is small and can be corrected for by the aid of this formula, yet it cannot be neglected. It may be noted that if we let $R=-1$, this becomes, as it should, the standard formula for the determination of P_a by means of the wet and dry bulb thermometer.

Conclusion

If we put in the form of an equation Mr. Cummings'[1] statement of the relation between evaporation and radiant energy, we have

$$I=S+LE+K \tag{25}$$

[2] Since the above was written, a somewhat similar formula has been derived empirically from wet and dry bulb data. D. K. Dean, Power **62**, p. 754 (1925).

where I is "the radiant energy . . . . integrated over any time interval" or perhaps a little more explicitly, the solar and sky radiation corrected for reflection, minus the back radiation, S is the "heat represented by the change in temperature of the water," LE is "the heat represented by the evaporation (E) during the same time interval," L, of course, being the latent heat of evaporation, and K is a "relatively small correction" to cover other losses. These other losses, however, are due to conduction and convection which we have put equal to R times the losses by evaporation, i. e., $R(LE)$, where R can be determined by Eq. (24). Substituting this value of K in (25) we have

$$I=S+LE(1+R) \qquad (26)$$

which is an exact equation for any body of water that is thermally insulated on the sides and bottom (a condition holding for most lakes) since it takes into account all processes by which heat can be lost or gained.

Consequently if we know S, E and R, which can be determined easily in any small insulated test jar, we can, following the method proposed by Cummings[1] use this slightly modified formula (26) to determine I or, vice versa, if we know I and can measure S and R, we have a means for calculating the evaporation E from a large body of water where it cannot be measured directly.

Such a body of water, however, is very nearly a black body over a very wide range of wave-lengths, since throughout the infrared even a thin layer of water absorbs almost completely, while in the visible this is true if the water is deep enough, as in a lake or if the inside of the vessel is properly blackened, as can be easily done for any test jar. In addition the reflection at the surface due to the difference in index of refraction is small throughout the visible and infrared to 20μ,[3] which is well beyond the maximum of the back radiation. On account of this fact I as determined by Eq. (26) becomes at once, with only a very small correction for reflection, the value of the net radiation exchanged with a black body at the temperature of the water. Thus such a jar of water can be used to determine the net heat radiated by a black body at night or received by it during the day time.

In a succeeding article Mr. Cummings will present the results of experiments designed to check the modified form of his equation, Eq. (26), under a series of widely different condition. Since this Eq. (26) depends on the determination of R as given by Eq. (24), these experiments will

[3] Rubens and Ladenburg. Verh. d. Phys. Ges. **11**, 16 (1909).

also serve as a test of Eq. (24) as well. His preliminary experiments indicate that these equations will be verified completely.

In conclusion the writer wishes to thank Professor Epstein for his derivation of Eq. (11).

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
March 12, 1926.

HEAT TRANSFER IN THE ANNULAR SPACE BETWEEN TWO COAXIAL CYLINDERS*

By S. R. Parsons

Abstract

Two brass tubes are mounted with a common axis, one inside of the other, and are warmed by driving hot air, in turbulent flow, through the annular space between them. The rates of transfer of heat to the two tubes are compared by means of a coefficient representing heat transmitted per unit time per unit area of metal surface per unit difference of temperature between metal and air. Lees has shown that in streamline flow there would be a difference in the surface friction per unit area for the two tubes, and if that were true in turbulent flow, there would be a corresponding difference in the coefficients of heat transfer. The experimental results show that if there is such a difference in turbulent flow, it is not of the magnitude to be expected from Lees' equations, and fail to show with certainty that any difference exists.

WHEN air is passed through the annular space between two coaxial cylinders, such as that formed by one metal tube inside of another, the stream acts simultaneously on two surfaces, of which one is convex, and the other concave. Lees[1] has shown that when a fluid passes in streamline flow through such an annular space, the surface friction per unit area is less on the outer tube than on the inner one, and he raises the question whether there is a similar difference in turbulent flow. If there is, there should be a corresponding difference in the rates of transfer of heat between the stream and the two surfaces, which might be interpreted as representing a difference in the character of the flow close to the walls,—that is, a difference in the extent to which the stream may be regarded as scouring the surfaces. The purpose of the work described in this paper was to show whether or not heat is transmitted more readily to one of the two surfaces than the other.

Apparatus and Experimental Procedure

Two pairs of brass tubes were used, the first 91.3 cm in length, and the second, 170.0 cm. The inner and outer diameters of the annular spaces were 0.949 and 1.706, and 0.950 and 2.307 cm, respectively. Each tube was about 1 mm in thickness. Air from a compressor connected to a large tank was forced through a brass tube 1.7 cm in diameter, in which its speed was estimated by means of a Pitot tube; then through a

* Research Paper No. 36, Journal Series, University of Arkansas.

[1] C. H. Lees, Proc. Roy. Soc. 92, p. 144 (1915).

brass tube surrounded by a heating coil; and then into the annular space between the experimental tubes, which were mounted in a vertical position in order to avoid the sag that would be inevitable if they were horizontal. The outer tube was set into a block of wood, through which a hole was bored to admit the air. A circular wooden plug was fitted into the end of the inner tube, the lower end of the plug being smoothed off into a streamline form, to direct the air as gently as possible into the annular passage. This plug supported the weight of the inner tube, and was itself centered and held in place by fine piano wires passing out through small holes in the wooden block, and wound on screws for adjustment. A thermocouple junction was set in the center of the air stream a few centimeters below the plug. A similar arrangement for centering the plug was used at the upper (outlet) end, and a second thermal junction was placed in the center of the stream about 5 cm above the top of the plug. The air passage ended in a bell mouth. A wooden box about 12 cm square was placed around the tubes, to minimize the effects of air currents in the room. Thermometers were inserted through one side of the box, and while no attempt was made to render it air tight, it was found that the rate of cooling of the outer tube to the air was not appreciably affected by currents in the room, and could therefore be computed with satisfactory accuracy for any condition obtained in the experiments.

Thermal junctions were soldered to the outside of the outer tube, and corresponding junctions attached opposite them on the inner tube, at points whose locations appear in the table below. Holes were drilled in the inner tube, and the junctions soldered into these holes flush with the surface, which was then filed down to as near its original condition as possible, the wires being brought away in a cable inside of the tube to its upper (downstream) end, from which they were led to the measuring instruments. The electrical connections were such that each couple could be connected to a potentiometer, or directly to a galvanometer.

The rates of transfer of heat from the stream of air to the two tubes were compared by means of the rates at which their temperatures rose, and in order to obtain simultaneous rates, two galvanometers were used, one for each tube. The galvanometer readings were calibrated against the potentiometer after each run. A metronome was set to beat seconds, and to ring a bell every third second, and readings of the two galvanometers were taken alternately on the stroke of the bell. From these readings, the temperatures of the two tubes were computed, and plotted against time.

Method of Computation

Considering any point along the tubes, and using for temperatures the mean values in a plane perpendicular to the axis of the tubes and including the point considered, we may write the equation for either tube alone

$$ms\frac{d\theta}{dt}=q(2\pi r)(T-\theta)$$

where θ is the temperature of the tube; T, the temperature of the air stream; m, the mass per unit length of the tube; s, the specific heat of the tube; r, the radius of the tube; t, the time; and q, the surface coefficient of heat transfer, in units of heat per unit time per unit area per unit difference of temperature between air and tube. The experiments yield values for all of these quantities except q and T. It is not feasible to measure the air temperature T inside of the annular space because, aside from the difficulties of measuring the temperature of a stream of gas at a point where its temperature is changing, anything even so small as thermocouple wires placed in the stream might affect the character of the flow enough to destroy their value. These temperatures may be eliminated, however, and a comparison of the coefficients q for the inner and outer tubes may be obtained as follows. The equation above is applied to each tube, and the values of θ and $d\theta/dt$ are obtained at two different instants during each experimental run. Then, if we let θ be the temperature of outer tube, ϕ the temperature of inner tube, subscripts o and i represent outer and inner tubes, and subscripts 1 and 2 represent the first and second sets of values, respectively, we may write four equations:

$$m_0s_0(d\theta/dt)_1=q_0(2\pi r_0)(T_1-\theta_1)$$
$$m_0s_0(d\theta/dt)_2=q_0(2\pi r_0)(T_2-\theta_2)$$
$$m_is_i(d\phi/dt)_1=q_i(2\pi r_i)(T_1-\phi_1)$$
$$m_is_i(d\phi/dt)_2=q_i(2\pi r_i)(T_2-\phi_2)$$

Solving these equations for the ratio between the coefficients q, and for simplicity letting $(d\theta/dt)_1=a_1$, $(d\theta/dt)_2=a_2$, $(d\phi/dt)_1=b_1$, and $(d\phi/dt)_2=b_2$, we obtain

$$\frac{q_0}{q_i}=\left(\frac{m_0s_0r_i}{m_is_ir_0}\right)\frac{b_1(\phi_2-\theta_2)-b_2(\phi_1-\theta_1)}{a_1(\phi_2-\theta_2)-a_2(\phi_1-\theta_1)}.$$

Since the outer tube is losing heat to the surrounding air while its temperature is rising, the value of $d\theta/dt$ used in the equations will be greater than that obtained from the graphs by an amount given by the

equation $d\theta/dt = -kT'$, in which T' is the difference in temperature between the tube and the surrounding air, and k is a constant determined from the rate of cooling of the tube when the air is not flowing through it. While the four equations given above suffice for a solution of the temperatures T_1 and T_2 of the air as it passes any thermal junction, the form of the algebraic solution is such as to magnify the effects of expermental errors, and the results are of little value.

The speed of the air stream was estimated from the readings of the Pitot tube, from the ratio of the cross sectional areas of the air passages at the Pitot tube and in the annular space, and from the estimated densities of the air at these two points. These speeds, and the temperature of the air at the entrance to the annular space, which was taken from the thermal junction located at the entrance, do not enter into the computations, but are tabulated with the results to show the range of conditions used in the experiments. The critical speeds for the two pairs of tubes were computed from Lonsdale's equation,[2] for a temperature of 100°C, and it will be seen that the speeds used were high enough to insure turbulent flow.

Results

The results are summarized in Table I. Preliminary trials failed to show any appreciable effect of slight changes in the centering of the inner tube, and if there is such an effect, it is probably balanced out in the mean of the results, on account of the locations of the various thermal junctions, which are as shown in the table, the azimuth representing angular distance around the axis of the tubes, measured from an arbitrary plane. If in smoothing off the inner tube after attaching the thermal junctions to it, the tube was not left in its original condition, any irregularities due to this cause will also tend to balance each other.

Whether there is any significance in the fact that the ratio of the coefficients appears to be less at points near the outlet of the tubes than near the entrance, the writer can not say. The nearest points used are respectively 52 and 66 times as far from the entrance as the thickness of the annular space, for the two pairs of tubes.

For these pairs of tubes, the equations of Lees for streamline flow give values of 0.70 and 0.74, respectively, for the ratio of the surface friction per unit area on the outer tube to that on the inner tube; and since the rate of transfer of heat is proportional[3] to the surface friction, the same values would represent the ratios of the coefficients q. The

[2] T. Lonsdale, Phil. Mag. **46**, p. 163 (1923).

[3] Great Britain Committee for Aeronautics, Technical Reports 1912–1913, p. 45.

table shows that over something of a range of speeds and temperatures the mean ratio of the coefficients q is slightly greater than unity, indicating that if there is a difference in the heat transfer coefficients for turbulent flow, it is not comparable with that for streamline flow. But while this mean ratio is a little greater than unity, it must be

TABLE I

Values of the ratio, q_o/q_i, of the rates of transfer of heat to the outer and inner tubes.

Location of thermal junction distance from entrance	azimuth	Speed of air stream	Air temperature at entrance	$\frac{q_o}{q_i}$
First pair of tubes: length 91.3 cm; thickness of annular space, 0.38 cm; critical velocity, 7.9 m/sec.				
20 cm	0°	14.4 m/sec.	148°	1.23
20	0	14.4	148	1.18
35	90	21.7	122	1.21
35	270	12.6	150	1.15
55	0	11.9	142	.90
55	180	17.7	113	.99
75	270	24.0	136	1.01
				Mean 1.08 ± .10
Second pair of tubes: length 170.0 cm; thickness of annular space, 0.68 cm; critical velocity, 4.9 m/sec.				
45	90	6.7	132	1.01
60	270	7.3	122	.97
60	270	7.3	118	1.12
60	270	11.9	121	1.21
60	270	11.9	119	1.13
60	270	6.0	119	1.12
135	0	6.3	118	.98
135	0	9.7	133	.97
135	0	6.9	159	.91
135	0	6.9	158	.92
				Mean 1.03 ± .09

admitted that the experimental errors are large, and that the results do not show with certainty that the coefficients for the two surfaces are not identical. In other words, the experiments fail to show any difference in the character of the turbulent flow close to the two surfaces.

THE UNIVERSITY OF ARKANSAS,
February 12, 1926.

BOOK REVIEWS

Relation between temperature, pressure, and densities of gases (S. F. PICKERING), CIRCULAR OF BUREAU OF STANDARDS, No. 279.—This is a compilation of the known pvT relations of the familiar gases with a discussion of the equations of state of van der Waals, Dieterici, and Berthelot. The numerical use of the tables and curves, as well as of the equations, is explained in detail in the simplest possible terms. Many tables are given so that the Circular contains sufficient information for the solving of problems in this field. A very extensive bibliography is included. The circular should be extremely useful to users, commercial and scientific, of these gases, as well as to teachers. 190 pp., Government Printing Office, Washington, D. C. 1926. Price 25 cents.

J. R. ROEBUCK.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE WASHINGTON MEETING
APRIL 23 AND 24, 1926

The 139th regular meeting of the American Physical Society was held at the Bureau of Standards, Washington, D. C. on April 23 and 24, 1926. The presiding officers were Professor Dayton C. Miller, President of the Society, and Professor K. T. Compton, Vice-President. The attendance was about three hundred.

On Friday evening there was a dinner at the Raleigh Hotel, attended by two hundred and thirteen members and guests. The speakers at this dinner were Professor M. I. Pupin, Dr. S. W. Stratton, Dr. G. K. Burgess, and General G. O. Squier.

Meeting of the Council.—At the meeting of the Council held on April 23, 1926, seventeen were elected to membership: Martin J. Connoly, Kenneth Cole, Austin M. Cravath, C. del Rosario, Karl G. Emeleus, Hugh Farrell, Sylvan Harris, L. G. Hector, D. W. Morehouse, Leonard J. Neuman, Nicolas P. Rashevsky, P. N. Rhodes, Clarence Rockwell, John L. Rose, Shou Chin Wang, George P. Welch and Harvey A. Zinszer.

The regular program of the American Physical Society consisted of ninety-four papers, Numbers 2, 7, 9, 61, 73, 86, 87, 89, 90, 91, 92, and 95 being read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary.

ABSTRACTS

1. A precision study of the K absorption limit. F. K. RICHTMYER and J. B. BISHOP, Cornell University.—A series of careful measurements of *observed* absorption coefficients taken through the K absorption limit of silver yields data which, after correcting for the finite width of the slits, are in agreement with the assumption that the λ^3 law holds up to the limit from both directions and at the same time furnishes a method for determining, with comparatively high precision, the magnitude of the absorption discontinuity.

2. The effect of chemical combination on the absorption of x-rays. W. B. MOREHOUSE, Cornell University.—The x-ray absorption by aqueous solutions was measured

before and after chemical reaction, employing a differential null method similar to that described by Becker (Phys. Rev., **20,** 134, 1922), and using the direct beam from a water cooled Molybdenum Coolidge tube, operating at 30 kv peak. Cells having equal compartments were used, so that the same elements were in the beam before and after combination. Measurements were made on the following reactions:

(A). $3KI+I_2+2Na_2S_2O_3 \rightarrow 3KI+2NaI+Na_2S_4O_6$.

(B). $K_2Cr_2O_7+12KI+14HCl \rightarrow 8KCl+2CrCl_3+7H_2O+3I_2+6KI$.

(C). $NaOH+HCl \rightarrow NaCl+H_2O$.

Corrections having been made for changes in density the results indicate: Reaction (A). The mass absorption coefficient of the solution after reaction is approximately 0.25 percent less than before reaction. Reaction (B). 0.25 percent greater. Reaction (C). No appreciable change. Since iodine, sulphur and chromium are the only elements changing valence and since computations from known absorption coefficients show that the absorption by the iodine in the beam is several times that by either the sulphur or the chromium, it seems probable that the absorption by iodine in the free state is greater than its absorption in the combined state.

3. X-ray absorption in heated silver. H. S. READ, National Research Council Fellow at Stanford University.—Previous research (Phys. Rev., April, 1926) has suggested that Al, Fe, Ni, Cu, Ag, and Pb have slightly larger absorption coefficients at higher temperatures. Total radiation from a tungsten target tube was used. Continued work with Ag indicates that the transmission is a complicated function of the wave-length (0.2 to 0.7A used) increasing with temperature at some wave-lengths and decreasing with temperature at others. The largest change was a 1.5% decrease in transmission at the K-limit when the Ag strip was heated to 830°C. If this were due to a shift of the K-limit the shift corresponds to +0.00021A which corresponds in turn to −11. volts. This result suggests that energy of thermal agitation may add to x-radiation energy or that heat prepares the atoms in some way to absorb slightly smaller quanta, at the K-limit, than is possible when cool. An equal shift of the whole absorption coefficient curve does not appear to account for the changes of transmission at some of the other wave-lengths. A correction was made for the effect of thermal expansion. A detailed account of the method and results will be published.

4. Conditions for the disappearance of the unmodified line in the Compton effect. G. E. M. JAUNCEY and R. A. BOYD, Washington University. The method previously described by Jauncey and DeFoe (Phys. Rev., **27,** 102, (1926)) for measuring the ratio of the modified to total scattering coefficients when a wave-length of 0.41 A is scattered by carbon at various angles has been used. The ratio becomes practically unity at 87° and continues unity for angles out to 120° (we did not test it further out). However, at angles less than 87° there is a rapid decrease of the ratio as the angle decreases. It seems therefore that unmodified scattering disappears at 87° when $\lambda=0.41$ A. On Jauncey's theory, unmodified scattering disappears at 82°. There is thus good agreement with theory.

5. Measurement of x-ray scattering coefficient. PIERRE MERTZ, Cornell University.—The mass scattering coefficient was measured directly by collecting the scattered radiation in an ionization chamber surrounding the scatterer, comparing its intensity with that of a portion of the primary beam going through an auxiliary ionization chamber of equal length along the ray path. The primary beam consisted of the continuous radiation from a Coolidge tungsten tube, filtered through Al and Cu until the spectral width between the half-maximum intensity points was about 25% of the mean wave-length. Corrections were made for internal absorption in the scatterer and for the increased absorption of the scattered beam in the ionization chamber due to the Compton effect. The latter could not be estimated very accurately and is probably one

of the largest sources of error in the determination. The values of mass scattering coefficient (σ/ρ, in cm²/gram) as determined are given below:

λ	.32	.43	.54	.66	.79 A.
Scatterer			σ/ρ		
C	.166	.182	.194	.214	.234
H_2O	.198	.206	.210	.216	.228
Na	.173	.191	.248		
Li	.133	.165	.157	.169	.200
B	.154	.162	.169	.165	.179

6. Intensity of x-ray reflecion from solid and powdered sodium chloride. J. A. BEARDEN, University of Chicago. (Introduced by Arthur H. Compton.)—The experiment of the intensity of x-ray reflection by Bragg, James and Bosanquet has been repeated using monochromatic x-rays (Kα line of Molybdenum reflected from rock-salt crystal) for all orders of reflection thereby reducing the uncertainty in choosing a base line. The values of the structure factor F are in satisfactory agreement with the values obtained by the previous experimenters. The most uncertain elements entering in these experiments are: (1) the linear absorption coefficient and (2) the extinction effects. Measurements of the intensity of reflection from powdered crystals have also been made with monochromatic x-rays, using both the transmission and the reflection methods. Both powder methods gave the same values for the structure factor F for several samples of sodium chloride of different history. Except for the (100) plane, however, the values were consistently higher than the corresponding values obtained by the solid crystal method.

7. Refraction of x-rays by method of total reflection. RICHARD L. DOAN, University of Chicago.—The critical angle of total reflection of x-rays from polished surfaces is related to the index of refraction by the expression $\theta_c=(2(1-\mu))^{\frac{1}{2}}$, θ being the glancing angle of incidence. Since this critical angle has been found experimentally to be sharply defined, this method furnishes a simple means of determining indices of refraction with a relatively high degree of accuracy. The line MoKα_1, isolated by means of a calcite crystal and suitably placed slits, was allowed to fall on optical surfaces of speculum metal and glass, the reflected beam being received on a photographic plate one meter distant. Approximately one hundred one-minute exposures were made as the mirror was turned at intervals of a few seconds of arc through a total range of about 7′. Measurements, accurate to 1%, gave for speculum, $\theta_c=10'52''$, $1-\mu=4.96(10)^{-6}$; for glass, $\theta_c=6'18''$, $1-\mu=1.67(10)^{-6}$. Attempts were made to use sputtered gold films for reflecting surfaces but the reflection was surprisingly weak and the critical angle not sharply defined. An accurate measurement of the index of refraction of MoKα_1 in gold would be valuable as a check on the Drude-Lorentz dispersion formula because of the expected large resonance effect due to the L-electrons.

8. Refraction of x-rays in prisms. BERGEN DAVIS and C. M. SLACK, Columbia University.—*A continuation of measurements of refraction of x-rays by means of a double x-ray spectrometer* (Phys. Rev. **27**, 18, (1926)). The double x-ray spectrometer is well suited to this purpose, since the position of the peak of the rocking curve is not affected by unsymmetrical absorption in the prism. Measurements of δ, ($\mu=1-\delta$) were made in substances tabulated below with the observed value in brackets. Using Mo Kα ($\lambda=$ .7078) the values of $\delta\times10^6$ are: Ag (5.85), Cu (5.95), S (1.39), Al (1.68), Carbon (graphite) (1.23), celluloid (.98) and paraffin (.7). Using CuKα (1.537), the values of $\delta\times10^6$ are: Al (8.4), celluloid (4.78) and paraffin (3.28). These results agree well with the values calculated. *Broadening of rocking curves.*—The rocking curves were much broadened when the rays passed through granular substances such as graphite, grated paraffin, etc.

This effect, which appears to be due to refraction by the successive particles, has been treated theoretically by Dr. R. van Nardroff. A formula has been obtained which permits the calculation of the size of the particles from the observed broadening.

9. The refraction of x-rays applied to the determination of the diameters of small particles. ROBERT VON NARDROFF, Columbia University.—The divergence introduced into a beam of x-rays on passing it through a mass of refracting particles is investigated mathematically. It is found that a plane beam would be scattered by a single sphere of index of refraction $\mu=1-\delta$ so that the fraction of the energy in a cone at an angle between ω and $\omega+d\omega$ with the original direction is $8\delta^2\omega d\omega/(4\delta^2+\omega^2)^2$. For a large number of spheres, if n is the average number of spheres passed through by a ray, the root mean square bend produced is $\alpha_0=2\delta[n(\log 2/\delta+1)]^{\frac{1}{2}}$ and the fraction of the energy lying in a cone between α and $\alpha+d\alpha$ is $2\alpha(\exp.\ (-\alpha^2/\alpha_0^2)\ )/\alpha_0^2$. For a beam originally having a width at half maximum W_0 as measured on the rocking curve of the second crystal of a double x-ray spectrometer, the width after passing through the refracting material will be $W=(W_0^2+2\alpha_0^2)^{\frac{1}{2}}$. This gives a means of determining the number, and, if the total mass is known, the size of particles which could not be measured by other methods. The method is applied to rocking curves obtained by Davis and Slack for beams passed through different thicknesses of graphite. The variations of curve width with thickness of graphite are found to be in agreement with the theory, and, assuming the particles acted like spheres, their approximate diameter is found to be .0035 cm.

10. The theory of x-ray dispersion. R. DE L. KRONIG, Columbia University.—The quantum theory of dispersion as developed by Ladenburg and Kramers is extended so as to apply to the refraction of x-rays, where the number of atoms in a wave-length cube is no longer large, and the absorption forms a continuous band. A general formula for the index of refraction in terms of the atomic absorption coefficient α and the critical frequencies is given. From the condition, experimentally verified, that the electrons in the atom for impressed frequencies, large compared to their natural frequencies, shall act like free electrons as far as the index of refraction is concerned, a relation is obtained for α. The theory is in accord with Heisenberg's quantum mechanics. Some considerations on the origin of the Compton shifted radiation are added, from which it appears that in the wave description this radiation must be regarded as coming from all the atoms and as being coherent with the incident waves; a result suited to stress the difficulty of harmonizing the wave picture with that of quantum processes in the atoms.

11. The polarization of characteristic x-rays. J. B. BISHOP, Cornell University.—An investigation to determine a possible state of polarization of the alpha lines of molybdenum was undertaken in the following manner: A molybdenum target water-cooled Coolidge tube was so mounted that it could be rotated about an axis perpendicular to the cathode stream and passing through the focal spot. A carbon block was placed in the path of the x-ray beam and the intensity of the radiation from it was measured parallel to and perpendicular to the cathode stream respectively as the tube was rotated. A second ionization chamber receiving a portion of the direct beam was used in order to detect a possible variation of intensity of the incident radiation due to improper alignment and fluctuations of the current through the tube. When a zirconium filter, which is relatively transparent to the alpha lines, was used; it was found that the ratio of the intensity of radiation scattered parallel to the cathode stream to that scattered at right angles to the cathode stream was about 0.74. On using a strontium filter, which strongly absorbs the alpha lines, this ratio was about 0.84. One concludes from these results that the alpha lines are at least partially polarized.

12. An electron lattice theory of metals. BERTRAM E. WARREN, Massachusetts Institute of Technology.—Metallic crystals are built up of positive ions and of electrons,

both the ions and the electrons arranging themselves in a definite space lattice. The particular type of lattice utilized must represent a minimum of potential energy, and therefore depends on the number of valence electrons given up by each atom. The heuristic rule is laid down that atoms with one or two valence electrons will lose them, while atoms with more than two will lose only those in excess of two. The metals of Group I and III should utilize a complete lattice of the rock salt type, the sub-lattice of the positive ions being face centered cubic. In exception to this, the sub-lattice of the alkalies must be considered as face centered tetragonal. The sub-lattice of the metals of Groups II and IV should be either face centered cubic or hexagonal close packed. Groups V and VI should utilize a sub-lattice of the body centered cubic type. The lattice of a Group VII metal should not be of any of the simple types. These predictions are in very good agreement with the results of x-ray determinations. Such physical properties as the good ductility and conductivity of the face centered metals, and the high melting points of the body centered metals would be expected. The metals of Group VIII have not been classified.

13. The carbon atom model and the structure of the diamond. R. B. LINDSAY, Yale University.—Using a method similar to one previously described by the writer the 2_1 orbits in neutral carbon are approximately computed, introducing the assumption that the four orbital planes are arranged in tetrahedral symmetry. The atoms are then distributed in the diamond lattice and the field on any electron due to its own atom and neighboring atoms is calculated as a function of the distance from the nucleus assuming that: (1) the orbital plane of the electron is oriented in a certain symmetrical way relative to the lines joining its nucleus to those of the neighboring atoms; (2) for a first approximation only the four nearest atoms may be considered as effective; (3) the effect of the electrons in the neighboring atoms is that due to a time distribution of their charges in their orbital planes, disregarding definite phase relations such as have been assumed by previous writers. An approximate expression for the increase in energy of the electron orbit due to the neighboring atoms is developed, and the calculation of the lattice energy per electron for various values of a, the lattice constant, is carried out. The equilibrium value of a comes out between 1.10A and 1.60A (nearer the latter). In fact the heat of sublimation for $a=1.50$A is found to be 161 calories per mol. The accepted experimental values for these quantities are $a=1.54$A and $Y=168$ to 177 calories per mol. Compressibility calculations for this model are being undertaken.

14. The crystal structure of zirconium oxide. WHEELER P. DAVEY, General Electric Company.—ZrO_2 appears to crystallize in several forms. Using the powder method, diffraction patterns of two of these have been interpreted. One type shows that ZrO_2 may exist in a face-centered cubic lattice of ZrO_2, $a=5.098$A. The strong lines of the pattern taken alone show a diamond cubic pattern, indicating that the Zr^{++++} and $2\ O^{--}$ are situated in the lattice like Ca^{++} and $2\ F^-$ in CaF_2. The second type of diffraction pattern shows that ZrO_2 may exist in a triangular close-packed lattice of ZrO_2, $a=3.598$ and $C=1.633$. This structure is closely related to the face-centered cube. Both structures give a density of 6.13 which is to be compared with 5.75 given in 1860 by Nordenskiold.

15. Nickel-chromium solid solutions. F. C. BLAKE and A. E. FOCKE, Ohio State University.—A complete series of nichrome alloys has been studied by the powder method of x-ray analysis and the amount of distortion of the nickel lattice by chromium substitution and of the chromium lattice by nickel substitution has been determined.

The influence of impurity due to the crucible in which the melt is made has been studied and the correct lattices free from such influence have been determined. Intermetallic compounds and allotropic forms have been the subject of special study.

16. The ultra and extra-ultraviolet spectrum of iron as developed by the inverse photo-electric effect. OTTO STUHLMAN, JR., University of North Carolina.—A three element vacuum tube of the commercial form VT-I, with p'atinum filament and iron grid and plate, was used. In series with the grid was a sensitive galvanometer and a variable potential whose negative terminal was connected to the negative end of the filament. A second circuit with the positive end of a battery connected to the plate and its negative terminal connected to the galvanometer served to keep the plate at a constant positive potential higher than the positive potential of the grid. As a result of critically accelerating electrons, emitted by the filament, towards the grid monochromatic radiations are emitted, which are reabsorbed by the grid resulting in photo-electric emission. Such emission and absorption interpretations are given the discontinuities which appear in the potential-current curves. They are evaluated by the usual $V\lambda = 12344$ relation. Using a work function for iron equal to 5.000 volts the following spectral regions were reproduced. Spark spectrum of iron (Exner-Haschek, Spectren Tabellen) pronounced lines between 2456 and 2213. New lines between 2211 and 2154. Millikan, Bowen and Sawyer's spark spectrum, including the spectral region investigated by Bloch, from 2152 to 880A. The spectrum is being extended beyond 200A.

17. The extreme ultra-violet spectrum of titanium. R. C. GIBBS, Cornell University.—Using one of the vacuum spectrographs at the Norman Bridge Laboratory of Physics, California Institute of Technology, photographs of the hotspark spectrum of titanium were obtained over the region from 192 to 1718A. By comparison with the data of previous workers in this part of the spectrum, it was possible to identify many of the lines obtained on the plates as due to other elements such as oxygen, carbon and silicon, many of which are present with every element used as electrodes. By placing a plate for titanium and one for some other element obtained with the same setting of the spectrograph face to face on the comparator it was possible to determine with considerable accuracy, by taking relative intensities and structure of line also into consideration, what lines were not due to titanium. All of the twenty-five lines reported within the above limits by Lang were found and about ninety additional lines. Careful focussing and the use of a very narrow slit made it possible to fix the wave-length to within .05A in the case of many lines obtained in the second order. On one plate it was possible to observe in the second order all seven components of the 834 oxygen line.

18. On the spectrum of argon. F. A. SAUNDERS, Harvard University.—The spectrum of argon in the extreme ultraviolet obtained by T. Lyman shows a very strong pair at λλ1048.26 and 1066.72, and many other lines, some as yet unidentified. Following Paschen's neon notation, this pair is a combination between a $1p$ level ($j=0$) and $2s_2$, $2s_4$. The known frequency-differences in the rest of the argon spectrum yield the terms $2s_3$ and $2s_5$, and many $2p$ terms are readily obtained, some of which combine with all four s terms, others with s_2, s_4 and s_5 only, as in neon. Three of the latter (presumably p_4, p_5 and p_3) are unexpectedly found to combine with $1p$, and produce strong lines (λλ941.39, 932.09, 919.80). The same combinations also produce lines, (though weaker) in neon (λλ, 662.84; 665.30; 667.46), not previously identified. For these lines j must change from 0 to 2; they are thus quite unconventional. They are produced with a mild excitation. Other pp combinations seem to be present, but are not yet firmly established (e.g. Argon λ946.95). Many other terms in the argon spectrum have also been found, and photographs have been taken in the ultrared, which are yielding data for a complete analysis of this spectrum.

19. The quantum theory of the Zeeman effect for band lines. E. C. KEMBLE, Harvard University.—Assuming an electronic angular momentum with fixed components σ and ϵ along and perpendicular to the axis of figure of a diatomic molecule,

the application of Bohr's postulates to the precessional motion in a magnetic field leads to the Zeeman term formula

$$E = E_0 + rh\Delta\nu_n(\sigma^2 + \epsilon(j^2 - \sigma^2)^{\frac{1}{2}})/j^2,$$

where r is the magnetic quantum number, subject to the usual selection principle, $\Delta\nu_n$ is the Larmor frequency j is the total angular momentum. The following qualitative inferences may be drawn: (a) The Zeeman pattern for lines adjacent to a band origin will normally be simple and the scale may be similar to that for an atomic line. (b) The outer lines of a band will have very complicated patterns, usually on a scale entirely too small to detect. (c) If the initial and final values of ϵ are different, the outer lines of a band will seem to be diffusely broadened in a magnetic field. (d) The direction of rotation for the Faraday effect in the neighborhood of a band line will frequently be different for the P and R branches of the same band. The theory agrees with the meagre experimental facts only in general qualitative features.

20. On the continuous spectrum of hydrogen. W. H. CREW and E. O. HULBURT, Naval Research Laboratory, Washington, D. C.—In a discharge tube filled with dry hydrogen at a moderate pressure (1 to 3 mm Crookes dark space) the striations near the negative end of the positive column have quite different colors, widths and spacing; the first is a vivid blue and narrow, the second or third is pinker and wider, the third or fourth bluer again, the remainder being pinker or whiter for the most part. Spectrograms showed that the first blue striation, i.e. the one next to the Faraday dark space, emitted the continuous spectrum of hydrogen in great purity, the Balmer and molecular lines being relatively feeble. In the other striations the continuous spectrum was weaker than the line spectra, and in the cathode glow, Crookes dark space, negative glow and Faraday dark space was absent. The intensity decrement of the Balmer lines appeared to vary in different parts of the discharge. With moist hydrogen the Balmer lines were bright and the continuous spectrum dim in the striations. These facts together with the positive the ray analyses of the ions in a hydrogen discharge by Smyth and Brasefield support the conclusion that H_3 is the source of the continuous spectrum of hydrogen.

21. The structure of the hydrogen molecule. H. C. UREY, Johns Hopkins University.—Recently Dieke and also Takahashi have arranged the Fulcher bands of hydrogen into single band systems with each band consisting of a zero branch. To these Dieke has added positive branches for the red bands and incomplete branches for the green bands. A study of these positive branches shows that they may be rather doubtful. Witmer has shown that the Lyman bands in the far ultraviolet have a similar structure. Since only one band system appears in each group it seems most reasonable to assume that the vibration quantum number does not change in these transitions and that therefore the molecule is symmetrical about the median plane. Since the bands have only zero branches the molecule must have no angular momentum in the electron system for otherwise the frequency of rotation of the nuclei would appear in the Fourier expansion of the electron motion and therefore positive and negative branches would appear. It seems necessary to assign the steady states involved to the *vibration* electron orbits of the median plane. This would give no first order Zeeman effect as required and a diamagnetic model for the normal state.

22. The structure of the hydrogen molecule ion. H. C. UREY, The Johns Hopkins University.—The energy levels of the vibrational model of the hydrogen molecule ion have been calculated including the energy contributed by the vibration and rotation of the nuclei. The calculated spectroscopic term is

$$\nu = -134899/n^{*2} - 9.37/n^{*4} + 5358n_4/n^{*3} + 107.6m_1^2/n^{*4} - 0.1767m_1^4/n^{*6},$$

where n^*, n_4, and m_1 are the quantum numbers conjugate to the electron coordinate, and the vibrational and rotational coordinates of the nuclei respectively. The applica-

tion of the correspondence principle to the model requires that $\Delta n^* = 1, 3, 5, \ldots$, $\Delta n_4 = 0$ and $\Delta m_1 = 0$ for transitions emitting light. Bands emitted from such a molecule should consist of single band systems, each band having a zero branch only. Exact agreement between theory and experiment has not been found.

23. P, Q, R combinations in the sodium hydride many-lined molecular spectrum. E. H. JOHNSON, University of Chicago.—A study has been made of the many-lined spectrum obtained from sodium arc in hydrogen in the region from λ5500 down to λ3800. Direct comparison of high dispersion plates shows an arrangement wholly different from that of the hydrogen secondary spectrum. Though at first sight there is little evidence of band structure, several groups of P, Q and R branches have been traced out by means of the combination principle. The $\Delta F(m)$ relations indicate the presence of a Kramers and Pauli effect. Preliminary values of $2B$ lead to a final moment of inertia of about 5.5×10^{-40} gm cm², which gives a nuclear separation of about 1.8×10^{-8} cm for a sodium hydride dipole. A detailed quantum analysis of the bands is included.

24. Half-integral vibrational quantum numbers and rotational energy data for the MgH bands. WILLIAM W. WATSON, University of Chicago.—The magnitude of the isotope effect in the λ5211 band is shown to agree exactly with the assumption that $n' = \frac{1}{2}$ and $n'' = \frac{1}{2}$, as demanded by the new quantum mechanics. The "zero-points" of this band system can be represented by the equation

$$\nu = 19217 + (1603.5\, n' - 34.75\, n'^2) - (1493.5\, n'' - 31.25\, n''^2)$$

where n' and n'' take on half-integral values from $\frac{1}{2}$ to $3\frac{1}{2}$. For the final state in the λ5211 band, the rotational energy can be represented by $F = Bm^2 + Dm^4 + Fm^6$ where $m = j + \frac{1}{2} - \epsilon$, ϵ having the approximate value 0.47. Kemble's formula, $\omega = (-4\, B^3/D)^{\frac{1}{2}}$ gives the vibrational frequencies in the ν_0 formula to within the experimental accuracy of the data. The values of ΔF for the initial state indicate the presence of a Kramers and Pauli effect. The results of a least square solution and the question of missing lines lead to the approximate value $\epsilon = 0.43$ for the initial state. A comparison with rotational energy data for the C+H bands is made.

25. Nitrogen Series in the ultraviolet. J. J. HOPFIELD, University of California. —Four new series, namely, two series of triplets probably converging to a common head and belonging to the quartet system, and two series of doublets also having a common limit and belonging to the doublet system, have been observed in nitrogen. The short wave-length lines of one of the triplet series are given accurately by the equation

$$\nu = 117353 - 109677(m + 0.845685 - 0.022749/m^3 - 0.026562/m^4)^{-2}$$

in which $m = 1$, 3 and 4 correspond to terms already observed by Kiess. $m = 2$ gives a new triple term, and $1S = 117353$ (14.48 volts) is the lowest energy level yet observed in neutral nitrogen. The two doublet series which begin with the previously known lines at λ1742 and λ1592 respectively have each been observed to three members. Their common limit is 98100 cm^{-1} (12.11 volts). The terms representing these series are linked to the doublet terms already observed through the lines at λ1742. The resonance and ionizing potentials of neutral nitrogen are contained in the data given above. Interseries and other relations are now being studied.

26. The infrared spectra of brucite and some sulphates; isotopic effect. E. K. PLYLER, University of North Carolina.—By means of an infrared spectrometer the structure of the absorption band of brucite [$Mg(OH)_2$] was studied. The region of greatest absorption was found to be at 2.48 μ. Besides this maximum there were small maxima of absorption located at 2.40 μ, 2.30 μ, 2.14 μ. The maxima at 2.48 μ, 2.40 μ, and 2.30 μ correspond approximately in position and absorption to the isotopes of Mg^{24}, Mg^{25},

and Mg^{26} as found by Aston. The small band at 2.14 μ, corresponds in position to Mg^{28}. However this isotope is not given. The work of Coblentz has been examined for the isotopic effect. In the reflection spectrum of nickel sulphate in solution there are two maxima located at 9.15 μ, and 9.50 μ. The second is more intense. These maxima are probably due to Ni^{58} and Ni^{60}. In the spectrum of potassium sulphate there are two maxima, one at 9.00 μ, and the other at 9.40 μ. The maxima at 9.40 μ is much more intense. These two maxima are probably due to K^{39+41} and K^{39} taken twice. Other sulphates in solution only showed one maximum.

27. The intensities of the lines in the HCl absorption band at 3.5μ. D. G. BOURGIN and E. C. KEMBLE, Harvard University.—Measurements of the absorption curves for the HCl band at 3.5 μ have been made by the writers with tube-lengths varying between 0.1 cm and 3 cm. From plots of the areas of the individual lines against tube-length the areas of the corresponding absorption coefficient curves have been determined. The measurements cover all lines between the tenth of the R branch and the sixth of the P branch. The results are in harmony with the formula previously derived by one of us (Phys. Rev. **25**, 1, (1925)) provided that the statistical weight series 1, 3, 5, 7, . . . is used as suggested by Fowler and Dieke (summation rule). The agreement between the results and the theory was within three percent of the intensity of the strongest line for all but two of the lines measured. From the shapes of the area-tube-length curves it may be inferred that the lines are very sharp, the center of the strongest lines being completely absorbed in the first few millimeters of absorption path. The variation in the shapes of the curves from line to line shows definite evidence of a rotational isotope effect.

28. Analysis of Wood's iodine resonance spectrum. E. C. KEMBLE and E. E. WITMER, Harvard University.—The resonance spectrum of I_2 excited by the broadened green mercury line consists of several series of doublets. According to Lenz each doublet is due to molecular transitions from a definite initial excited state to two different final rotational states. The different doublets in a series are due to different final vibrational states, the different series to a variety of initial states present because the exciting line covers a number of absorption lines coming from different absorption bands. Mecke has partially analysed some of the absorption bands in the red and has worked out empirical formulas for the frequencies of the resonance series. Kratzer and Sudholt have written out theoretical formulas for the resonance series in harmony with the observations and from Mecke's data have evaluated the moment of inertia of the molecule. Assuming that the nuclear rotational quantum numbers of the final states associated with each doublet differ by exactly two, the authors have revised and extended the work of Kratzer and Sudholt. We obtain the values 7.9×10^{-38} gm cm^2 and 11×10^{-38} gm cm^2 for the moments of inertia in the normal and excited states respectively. The large difference between these values locates the origin within three lines of the head.

29. The fluorescent and absorption spectra of iodine. F. W. LOOMIS, New York University.—The four series without linear terms found by Mecke (Ann. d. Phys. **71**, 104, (1923)) in Wood's spectrum of fluorescent iodine excited by the broad green mercury line are due to four lines of the band (26, 0); those with positive doublet interval to lines in the P branch. The P and R branches are the absorption series Ia and Ib found by Mecke in this region. The fluorescent lines are identified. This makes it posisble to pick out a series of pairs of lines with common m', and another with common m'' and hence to find $B_0''=0.03835$, $B'=0.02480$ cm^{-1}, $J_0=(7.21\pm.03)\times10^{-38}$ and the absolute values of m which turn out half-integral. Similarly, lines of Mecke's series II belong alternately to the P and R branches of band (27, 0) and the fluorescent lines are identified as are also the main lines in three of the four remaining fluorescent series. Wood's measurements of the magnetic rotation of six absorption lines show in every case the

"normal" direction of rotation for lines here assigned to a P branch and the opposite for R lines. These results demonstrate the existence of P and R branches in absorption, which Mecke has doubted, and confirm the Lenz theory.

30. On the polarization of fluorescent light from colloid solutions. PAUL FRÖHLICH, University of Chicago, (introduced by William W. Watson).—The partial polarization of fluorescent light from aqueous solutions of fluorescein, eosine, magdala-red, rhodamine 5 G, and rhodamine B extra, produced by dissolving in them more and more gelatine, gum arabic, or agar-agar; and in acetone solutions of the same substances by dissolving in them successively more celluloid, has been investigated. Three different wave-lengths of the plane polarized exciting light were used. It is found that the percent of polarization is successively increased from zero or a low value to a maximum, by dissolving in the solution a colloid. The maximum value will be reached in some cases with 60 percent, in others with 100 percent colloid in a solid film. The percent of polarization in the case of colloid solutions shows the same effects as in the case of non-colloid solutions with a high viscosity, such as glycerin or oils. It is increased by lower concentration of the dye, and by longer exciting wave-length. With dyes having shorter wave-length absorption bands (fluorescin, eosine), the wave-length effect proceeds at a slower rate than with solutions having longer wave-length absorption bands (magdala-red, rhodamine). By suitable choice of concentration and exciting wave-length, the maximum value of the polarization is about 35 to 40 percent.

31. Fluorescent exciting power and black-body radiation. E. H. KENNARD, Cornell University.—Suppose one quantum number n of an atom has normally the value n_1 while another m is statistically distributed by thermal agitation. Let absorption at frequency ν_x change n to n_2 and m from m_1 to m_2; and suppose that after this process thermal agitation is either (a) ineffective (then $m_2 = m_2$ below) or (b) completely effective in re-distributing m statistically. Suppose fluorescent emission of frequency ν_y then occurs while n changes back to n_1 and m changes from m_3 to m_4. Then the Einstein theory (1917) leads to the equations

$$\phi_{yz} = k_x \alpha_y u_y, \qquad \phi_{yz}/\phi_{xy} = \nu_y u_y / \nu_x u_x,$$

where ϕ_{yz} = fluorescent emission of frequency ν_y per unit volume excited by unit energy density at ν_x, α_y = absorption coefficient and u_y = black-body density of radiation for ν_y, and the factor k_x depends on ν_x but not on ν_y. These equations should hold for iodine fluorescence, n referring to the electron jump and m either to the rotation of the molecule or to the atomic vibration. For the second equation, restrictions (a) and (b) are probably unnecessary. Perhaps the equations will hold also for fluorescent solids and liquids; experiments are in progress.

32. Transformation spectra and the principle of essential indentity. E. L. NICHOLS and H. L. HOWES, Cornell University.—At their transformation points many incandescent bodies, particularly certain oxides, emit light over and above that due to their thermal state. The effect, although reversible, is most readily seen as a temporary flash up when a small mass of the substance is cooling. Through the spectroscope it may be seen to be selective. When the incandescent body contains a rare earth in solution, as activator, the *transformation spectrum* consists of narrow bands which appear suddenly in the field of view and melt away as the temperature falls below the transformation point. *These coincide with the fluorescence bands characteristic of the activator* or where that is not the case are members of the sets of equidistant components of which the fluorescence spectrum is composed. In other words, the fluorescence spectrum and transformation spectrum for a given activator are essentially identical and the principle of *essential identity*, hitherto applied to luminescence at ordinary temperatures is extended also to the luminescence of incandescent substances. (Nichols and Howes, Phys. Rev. **19**, 304 (1922).)

33. The form of the absorption bands in solutions of the organic dyes, and a relation between absorption and fluorescence. ERNEST MERRITT, Cornell University—It is assumed that the active molecule behaves as an electric doublet whose moment changes from μ_0 in the normal state to μ_1 when excited. In the field E due to the solute molecules the frequency for absorption, or emission, is then ν instead of ν_0, where $h\nu = h\nu_0 + (\mu_1 - \mu_0)E$. If thermal equilibrium is assumed the absorption coefficient α, which is determined by the distribution of the normal molecules, and the fluorescence F, determined by the distribution of the excited molecules, will be

$$\alpha = V(E)\exp(-\mu_0 h(\nu-\nu_0)/kt(\mu_1-\mu_0)), \quad F = F_0 h\nu\, V(E)\exp(-\mu_1 h(\nu-\nu_0)/kt(\mu_1-\mu_0)),$$
$$F/\alpha = F_0 h\nu \exp(-h(\nu-\nu_0)/kt),$$

where $V(E)$ is the volume within which the field (in the direction of μ_0) lies between E and $E+dE$, and F_0 depends on the duration of the excited state. If the solvent molecule is also a doublet, $V(E)$ is shown to be independent of ν through a considerable range, so that α is exponential on the long wave side of the band. This result is confirmed by experiment with uranine in water. Measurements, not yet of high accuracy, indicate agreement with the theory to within 10 percent in the value of F/α.

34. Gyromagnetic electrons and a classical theory of atomic structure and radiation. LOUIS VESSOT KING, F.R.S., McGill University.—A charged sphere in rotation with spin Ω_1 is deformed by translational velocity v into an ellipsoid of revolution, and as a result acquires the properties of a gyrostat in so far as precessional oscillations are concerned. The electrodynamic coefficients of inertia (A, C, C) are rigorously determined by integrating the magnetic energy throughout the space, within and without the ellipsoid whose deformation is considered to be physically real. It is shown that the frequency ν of precessional oscillation is given by

$$2\pi\nu = \Omega_1(C-A)/C = \Omega_1(c_1-a_1)\beta^2(1+b_1\beta^2+b_2\beta^4+\ldots.), \qquad (1)$$

and leads to the formula $h\nu = \frac{1}{2}m_0v^2$(2)for moderate velocities, where $m_0 = \frac{2}{3}e^2/a$ and $\beta = v/c$, the velocity of light being denoted by c. Remembering that a precessing electron has the properties of a small magnet, and therefore can radiate electromagnetically, equation (2) is the well-known photo-electric equation, while h becomes a fundamental constant of a rotating electron expressed in terms of spin by the relation $h\Omega_1 = \pi c^2 m_0/(c_1-a_1)$(3) where (c_1-a_1) is a numerical constant equal to $\frac{2}{5}$ for the simple model considered. The spinning deformed electron leading to equation (2) appears to give, on classical mechanics and electrodynamics, the key to radiation problems generally, and in the corresponding theory of atomic orbits yields the principal fundamental series formulae, as well as an adequate account of fine structure, Zeeman and Stark effects.

35. Light quanta and interference. A. J. DEMPSTER, University of Chicago. Experiments by W. Wien and by the author have shown that after 5×10^{-8} seconds the process of light emission from a radiating atom is practically complete. The energy from a glow discharge radiated in the helium line 4471 (decay constant 5.42×10^{7}) was measured by comparison with the intensity of the spectrum from a black body at a known temperature. The glow discharge was made so faint that 8.4×10^{-11} ergs or 19 quanta fell on the end of an echelon diffraction grating per second. With this intensity each light quantum must pass through the echelon separately. Interference patterns were photographed, showing the same appearance as with bright sources. In particular the characteristic double order image was photographed, indicating interference of rays that have passed simultaneously through the fifteen different steps of the echelon.

36. Effect of an electric field on the radiation from hydrogen atoms. K. L. HERTEL, University of Chicago. (Introduced by A. J. Dempster).—Canal rays were allowed to pass from a discharge tube through a small hole into an observation chamber which was kept at a very low pressure (.0005 mm of mercury). The luminosity from the rays died out rapidly as found by other observers. The light from the canal rays on first

entering the low pressure chamber was observed to be partially polarized, the component parallel to the bundle being the stronger. It was found that the polarization decreased with increasing distance from the opening, the rate of decrease of the polarization being greater than the rate of decrease of the intensity of the rays. When an electric field was applied across the bundle the polarization observed at right angles to the field behaved quite differently. The initial polarization altered very rapidly, and, at two millimeters beyond the opening, was reversed so that the component polarized parallel to the bundle was weaker than the other. This partial polarization then gradually decreased in the field at about the same rate as a polarization then gradually decreased in the field at about the same rate as a polarization observed without the electric field.

37. The effect of changing the conditions of excitation upon the time of appearance of certain spark lines of cadmium and zinc. J. W. BEAMS, National Research Fellow, University of Virginia.—The appearance of the spark lines of cadmium and zinc was studied in the two spectra produced when the same spark discharge passed between metallic electrodes in air and through the ionized vapor of the metallic arc, by a method previously described (Brown and Beams, J.O.S.A. & R.S.I., **11**, 11, (1925)). Each of the spark lines 4924, 4912 ($4d_{1,2}-4f$); 6103, 6021 ($4p_1-5d_1$), ($4p_2-5d_2$) of zinc and 5378, 5338 ($5d_1-4f_1$), ($5d_2-4f_2$) of cadmium were observed to appear simultaneously in both spectra. From this it is concluded that the sequence in the appearance of spectrum lines in the spark is predominantly an atomic phenomenon and practically independent of the characteristics of the spark discharge.

38. Intensities in spectra and the new quantum mechanics. FRANK C. HOYT, National Research Fellow, University of Chicago.—On the basis of the new quantum mechanics of Heisenberg and Born it becomes possible for the first time to obtain exact expressions for the intensities of spectral lines. If the intensities for the linear oscillator as given by Born (Zeit. f. Phys. **34**, 858 (1925)) are compared with those calculated on the basis of the older form of the theory it is seen that no one of the possible expressions which were previously proposed can be regarded as exact, provided the new theory is accepted. Computations from the new theory are shown to be in agreement with the relative intensities of the (01) and (02) bands in HCl.

39. The use of a cathode-ray tube for the transmission of speech. C. W. VAN DER MERWE, Washington Square College, New York University, (Introduced by H. H. Sheldon).—One of the chief defects of the "speaking arc" as used by H. Th. Simon in 1898 was its comparative failure to reproduce in a satisfactory manner high-pitched tones. This failure was obviously due to the thermal inertia of the arc. The minuteness of the mass of the electron, and for that matter of the atom, suggested the substitution of an ordinary discharge tube for the electric arc. A tube of special construction containing a trace of a mixture of helium and neon was used and the substitution met with marked success, the high notes coming through much more clearly than in the case of the arc, sibilants like "s" and "c" being distinguishable from one another and voices being recognizable. Quantitative comparisons confirmed the superiority of the tube over the arc, and with a current of only 10 milliamperes flowing through the former, it was possible to telephone a distance of 60 feet with the greatest ease. The key to the success of the "speaking tube" is the luminosity of the discharge, since the light from the glow has to be reflected to the receiver. The success of this essentially wireless telephone will therefore depend on the efficiency with which discharge tubes carrying large currents can be built.

40. Experiments on cathode sputtering. E. O. HULBURT, Naval Research Laboratory, Washington, D. C.—Experiments with the flying metallic particles sputtered from a cathode have yielded the following facts. The side of a glass plate away from the

cathode receives a film of metal as well as the near side. There is no critical relation between the position of the glass plate with reference to the boundary of the cathode (Crookes) dark space and the film received. Shadows on the metallic film, in some cases geometrical and in others more complex, are cast by diaphragms and obstacles. No evidence of the reflection of the particles from glass or metal plates was obtainable. The particles enter open-ended glass tubes only to a distance roughly equal to the diameter of the tube. Some of the particles leave the cathode surface normally and therefore may be focussed on to a glass plate by a concave (spheridal surface) cathode. The circular film thus formed, however, had an unexpected hole in the center. Likewise a cylindrical cathode, which should concentrate the film into a strip, did so, but the strip had a central line of no deposit. The explanation of the various effects is perhaps to be found in the different sizes, velocities and charges of the flying particles combined with the many complexities of the interior of a discharge tube. Experiments with twenty-two metals enable them to be classed according to their relative ease of sputtering.

41. Normal arc characteristic curves depend on the absolute temperature of the anode. W. B. NOTTINGHAM, Princeton University.—The characteristic curves for normal arcs in air have been found to follow $V=A+B/I^n$ where V is the potential drop, I the arc current, A, B, and n constants with n directly proportional to the temperature of the boiling point of the anode material. Since the publication of this equation (Trans. A.I.E.E. Jan. 1923, p. 12) it has been verified by Anderson and Kretchmar (Phys. Rev., **26,** 33, (1925)) for short platinum and tungsten arcs of small current intensity. Recent measurements on tungsten arcs 2.0 mm to 10.0 mm in length and for currents 1.0 to 10.0 amperes show the average value of n to be 1.38 indicating a temperature of 5250°K while for the six arc characteristics of lengths between 5.0 mm and 10.0 mm the value of n was found to be 1.34 which corresponds to a temperature of 5100°K and agrees exactly with the Langmuir calculation. (Phys. Zeit., **14,** 1273, (1913)). The ten points now located along the straight line $n=2.62(10)^{-4}T$ are

Anode	W	Pt	C	CuO	Al_2O_3	NiO	Ag	Pb	Sb	Bi
T° K	5100	4180	3770	2580	2480	2450	2370	1850	1710	1690
n	1.34	1.15	0.985	0.67	0.65	0.64	0.624	0.48	0.46	0.445

These observations indicate that there may be something more significant to the equation $V=A+B/I^n$ than simply a convenient empirical formula and should be recognized as an experimental fact to be explained by any comprehensive theory of the electric arc.

42. Collisions between electrons and gas molecules. IRVING LANGMUIR and H. A. JONES, General Electric Co.—By a method already described (Science, **59,** 380 (1924)) the volt-ampere characteristic of a cylinder surrounding a coaxial cathode in a gas at low pressure gives quantitatively the probability P (per cm of electron path) that the electron, of 50 to 250 volt energy, will make a collision of a specified type. Thus the collisions may be elastic (P_e) or inelastic (P_k) and the inelastic collisions include those that ionize (P_i) and those (P_r) that make the electron lose a definite energy corresponding to a resonance potential (E_r volts). The electrons that make elastic and resonance collisions are scattered by each such collision only through small angles distributed according to probability laws, θ_e and θ_r being $2/\pi^{\frac{1}{2}}$ times the most probable angle of deflection in degrees. The results for 100 volt electrons calculated for a gas pressure of 1000 bars at 20°C are

Gas	P_e	P_k	P_r	θ_e	θ_r	E_r
Hg	19.	33.	10.	14.	14	6.7
A	10.	14.	1.3	14	14	13.
He	1.4	2.7	0.9	26	20	20.
N_2	7.8	12.2	3.6	14	18	13.
H_2	4.8	7.1	2.8	14	15	12.

43. Collector characteristics in neon and helium. R. RUDY, Nela Research Laboratory.—After having passed for variable distances through neon at pressures from .01 to 1 mm Hg, 70-volt electrons were received upon a disk. With a retarding field of over 100 volts, only positive ions reached the filament; their number remained nearly unchanged as the collector was moved away for a distance of several cms, and then started to decrease. When the collector was given the potential of the cathode, it began to receive primary electrons, which caused a break in the characteristic. From the slope, their average energy could be determined for different positions of the collector and compared with the results deduced from the theory of the scattering of electrons. Even in inert gases, the loss of energy is considerable besides excitation and ionization, whereas it is often neglected in the work on activation and disappearance of gases in the electric discharge. As the pressure was increased, the break disappeared entirely; the collector was now in the "positive column" of the discharge; a strong increase in current occurred only when the anode potential was approached. With heavier discharge currents space charges (e.g. near the collector) disturbed the field and discontinuous changes were noted.

44. Hydrogenation of ethylene by excited mercury atoms. A. R. OLSON and C. H. MEYERS, University of California.—In a previous article, (J. A. C. S. **48**, 389 (1926)), we have shown that ethylene and hydrogen react to form ethane under the influence of excited mercury atoms. The rate of the reaction was found to be proportional to the square root of the partial pressure of molecular hydrogen when all other factors are kept constant, and therefore the primary reaction is $H_2 = 2H$. The atomic hydrogen then diffuses from the illuminated region into the body of the gaseous mixture where hydrogenation occurs. The addition of an inert gas such as nitrogen should lower the diffusion rate. This effect is in qualitative agreement with the increased brightness of the thallium lines in the presence of nitrogen as observed by Loria, and in the decreased reaction rate of water formation from oxygen and hydrogen in the presence of nitrogen as observed by Mitchell. In the present set of experiments a gaseous mixture composed of 2.5 mm of N_2, 4.5 mm of H_2 and 1.2 mm of C_2H_4 were circulated past the illuminated window. The rate of reaction was found to be the same, within experimental limits, as the rate for the same mixture without the nitrogen. Under these conditions any increase of reaction rate due to metastable mercury atoms, must be offset by a decrease of rate due to diffusion. The broadening of the absorption line of mercury due to the added nitrogen was investigated by an external filter containing mercury vapor and found to be negligible.

45. Measurement of the increase of metastable atoms in mercury with accelerating voltage. HELEN A. MESSENGER and HAROLD W. WEBB, Columbia University.—The "radiation" from mercury vapor excited in a four-electrode tube by electrons from an equipotential cathode was measured by the "photo-electric" current from the nickel plate which was not sensitive to λ2537 radiation. A quartz or a calcite window could be lowered at will into the space between the grids to cut off metastable atoms from the plate. With no window typical Frank and Einsporn curves were obtained showing all the breaks which they found. With quartz a similar curve was obtained above 5.2 volts although the current was reduced to 10% or less. Below 5.2 volts there was no measurable current. With calcite the currents were still smaller; the 5.7, 6.7, 8.05 and 8.35 breaks were missing. The difference between the "photo-electric" currents in the open tube and those obtained with quartz interposed measures the increase of metastable atoms with accelerating voltage. The difference between the quartz and the calcite curves shows the presence of λ2140 radiation and further shows that the λ1849 radiation increases linearly from 6.7 volts.

46. The formation of negative ions in mercury vapor. WALTER M. NIELSEN, Duke University.—The method used is similar to that of Mohler (Phys. Rev. **26**, 614, (1925))

Electrons, projected along the axis of a tube between two plates were prevented from scattering by a magnetic field of 350 gauss parallel to the axis of the tube. Negative ions formed by the attachment of an electron to a molecule or to an atom were removed by suitable potentials applied to the side plates. The remainder of the current reached a circular plate at the end of the tube. With a small field between the side plates, the negative ion current was just barely observable (1×10^{-10} amperes). With higher fields the ion current increased enormously, approaching saturation when the potential difference between the side plates was increased to between 3 and 4 volts. The negative ion current was of the order of 9×10^{-9} amperes. The total current was of the order of 1×10^{-7} amperes. The ratio between the negative ion and total current decreases with increase in the driving potential for low voltages, but increases at 2.7, 4.7, 5.5, and 8.8 volts. The cause of the break at 2.7 volts is not known. The breaks at 4.7, 5.5, and 8.8 volts are believed to be associated with the electronegative properties of the mercury atom having an electron in a metastable orbit. The total current increases rapidly with increase in the driving potential and decreases at 4.9 and 6.7 volts.

47. Resonance and ionization potentials in mercury vapor. C. W. JARVIS, Ohio Wesleyan University.—Measurements on the critical potentials in mercury vapor were made with two types of tubes: (1) a three-electrode tube by which both total and partial currents were observed; (2) Hertz differential tubes of several different sizes. The table shows the values obtained together with those calculated from the relation $Ve=h\nu$ and those reported by Franck and Einsporn.

Calc.	F. & E.	Author	Calc.	F. & E.	Author	Calc.	F. & E.	Author
1.26		1.23	5.28	5.32	5.22	7.69	7.73	7.74
2.26		2.21	5.43	5.47	5.37		8.05	8.02
2.83		2.80	5.73	5.76	5.70		8.35	8.33
3.37		3.44		6.04	6.05	8.81	8.86	8.82
3.70		3.80		6.30	6.46	9.32	9.37	9.33
4.16		4.21	6.67	6.73	6.79	9.52	9.60	9.58
4.66	4.68	4.53		7.12	7.13	9.80	9.78	9.90
4.86	4.90	4.97		7.46	7.41			

A number of critical potentials below 4.68 volts were observed. The interpretation of these is much in doubt, as they imply that in normal mercury vapor the valence electron is in a higher energy level than that corresponding to the ground orbit of the valence electron. Perhaps they may be attributed to the molecule of mercury.

48. The ionization potentials of hydrogen and nitrogen on an iron catalyst. GEORGE KISTIAKOWSKY, Princeton University, (Introduced by K. T. Compton).—By the method of electron bombardment, Gauger and Wolfenden showed that hydrogen adsorbed on nickel has radiation and ionization potentials characteristic of atomic hydrogen. Nitrogen adsorbed on a promoted iron catalyst has now been studied by an improved method. The catalyst was prepared by reduction in hydrogen and contained residual hydrogen. Ionization potentials in presence of nitrogen were found at 11.1, 13.0, 16.0, 17.1 corrected volts. The two highest doubtless belong to molecular hydrogen and nitrogen. 13.0 volts is slightly different from the ionization potential of gaseous atomic hydrogen, but evidently the energy required for ionization of an adsorbed gas atom is not necessarily the same as that for a free atom. This energy is compounded of the ionization energy of a free atom plus its adsorption energy minus the energy of adsorption of a free electron by the metal. The last two terms are not necessarily equal, though they are known for hydrogen to be not very different. The ionization at 11.1 volts was only observed when catalyst and nitrogen were both present and belongs, probably, to atomic nitrogen, whose gaseous ionization potential has been estimated spectroscopically as about 11 volts. Catalytic poisons were found to suppress the critical potentials at 11.1 and 13.0 volts.

49. Direct determination of the ratio of Planck's universal constant to the charge on the electron. ERNEST O. LAWRENCE, National Research Fellow, Yale University.—The precision of the method for critical potential measurements described at the Montreal meeting has been developed to a greater degree. The most recent determinations of the ionization potential of Hg vapor with assigned "weights" are:

Volts	Weight	Volts	Weight
10.46	8	10.36	5
10.32	4	10.40	4
10.42	10	10.44	4
10.37	10	10.39	10

Calculating in the usual way the mean value and probable error we have for the ionization potential 10.399 ($\pm$.007) volts. Applying the quantum postulate to the series limit there results for the ratio h/e the value 1.3735 ($\pm$.0009)$\times 10^{-17}$. Using Millikan's determination of e we have for h the value 6.550 ($\pm$.006)$\times 10^{-27}$, in which the error presumably is concerned with the uncertainty in e. These results are tentative pending the outcome of a thorough investigation of possible sources of systematic error.

50. On the threshold sensitivity of photographic emulsions to low speed electrons. KENNETH COLE, Cornell University, (introduced by F. K. Richtmyer).—A new design of magnetic dispersion electron spectrograph has been used in an investigation of the sensitivity of photographic emulsions to electrons of speeds below 100 volts. With commercial emulsions, the lowest speed that will produce a perceptible effect depends upon the emulsion and is usually in the neighborhood of 30 volts. It has been found however that a very thin film of lubricating oil on the surface of the emulsion enormously increases its electron sensitivity and at the same time lowers the threshold speed. With both oiled and unoiled emulsions, the photographic action seems to be due to fluorescence excited at the surface by the electron impact.

51. Secondary emissions from metals due to bombardment by high speed positive ions. WILFRID J. JACKSON, Princeton University, (Introduced by K. T. Compton).—A beam of K^+ ions from the iron catalyst source discovered by Kunsman was collected in a Faraday cylinder. A target could be interposed at the mouth of the cylinder by a magnetic control. The difference in current measured in these two cases gave the amount of the secondary emission. A transverse magnetic field could be applied at the target to prevent emission of electrons and thus separate electron emission from positive ion reflection. On bombardment of a molybdenum target which had been baked in *vacuo* to 1000°C and then exposed to air before final evacuation of the apparatus, secondary emission was inappreciable if the energy of the bombarding ions was less than 250 volts, was appreciable (1%) at 350 volts and rose steadily to about 9% at 1000 volts. These values depended somewhat on previous treatment of the target. After heating in position in vacuo by induced currents the emission fell to not more than a third of the above values. The secondary electrons were stopped by retarding fields of 0.25 volts. Positive ion reflection did not exceed 2%. Secondary emission from nickel was first detected at about 400 volts and increased to about 7% at 1000 volts.

52. Long wave length limit of mercury. WAYNE B. HALES, California Institute of Technology.—Kazda made the first definite and satisfactory determination of the critical potential and long wave-length limit for a clean flowing merucry surface, locating this critical frequency at 2735A with an uncertainty of $\pm$10A. Sophie Taubes' recent determination made on mercury drops suspended in argon was very much higher, namely, 3043$\pm$20A. I have, with completely new apparatus and new working conditions, found this long wave-length limit to be 2735A and have succeeded in getting a stationary surface so clean that the critical frequency has been found for it, namely, 2735$\pm$10A which is in entire agreement with Kazda for flowing mercury.

53. A new effect in the photo-electric emission from oxide-coated filaments. W. H. CREW, Naval Research Laboratory, Washington, D. C.—Total radiation from a quartz mercury arc was directed on to the oxide-coated platinum filament of a two-electrode quartz vacuum tube. Current-voltage curves were obtained with and without the light shining in the tube; and from these was determined the electron current due to the light alone. This current, plotted as a function of the plate voltage, increased rapidly to a maximum and thereafter fell off gradually. The position of this maximum was found to shift in the direction of decreasing potentials with increase of the temperature of the filament. Similar phenomena were observed with a filament made of oxide-coated tungsten, but could not be detected for either platinum or tungsten without oxide coating. The photo-electric emission was largely due to light of wave-length below λ3000A; for the photo-current was reduced almost to nothing by use of suitable glass absorbing screens, and was enhanced when mercury vapor was removed from the tube and the arc was water-cooled. The explanation of these phenomena is perhaps to be found in the changes in the surface of the filament under the action of the light rather than to space-charge effects.

54. The theory of thermionics. N. RASHEVSKY, Westinghouse Elec. & Mfg. Co., East Pittsburgh, (introduced by Dayton Ulrey).—The expression for the free energy of a metal is derived by computing the "Zustandsumme." Account is taken especially of the fact that the thermionic phenomena are essentially surface phenomena. The expression for the free energy thus obtained is substituted in the general formulas for thermionic emission previously derived. The final formula thus obtained gives indications for the understanding of the fact that while for pure metals the "A" constant of Richardson's equation has almost exactly the universal value postulated by Dushman, it has a largely different value for oxides and adsorbed films. The question as to the existence of an electric double-layer on the surface of a metal is discussed, as well as the influence of such a layer on thermionic emission. It is shown that while the existence of such a layer follows from Schottky's "Equilibrium Theorems," the same theorems lead to the conclusion that the temperature change of the moment of such a layer is relatively small. Its value may be approximately estimated.

55. Measurement of electronic charge by shot effect in aperiodic circuits. N. H. WILLIAMS and H. B. VINCENT, University of Michigan.—The theory of the probability variations of thermionic currents and their relation to the charge on the electron was investigated by Schottky. Hull and Williams measured the charge on electrons produced by thermionic emission, by photo-electric emission and by ionization of a gas. They worked with the high frequency currents set up in a tuned circuit by the Brownian fluctuations of the electron currents in a tube. The work here presented makes use of a five stage amplifier similar to the one they have described. The screen grid tubes were furnished by the General Electric Company. A pure resistance is substituted for the tuned circuit in which the shot effect is measured and an expression for the electronic charge in terms of the high frequency potential difference between the terminals of this resistance is developed. Both the mathematical derivation and the experimental procedure are considerably simplified. The results thus far obtained are in close agreement with the accepted value of the electronic charge. Measurements of shot effect have already thrown some light upon the nature of ionization and the mechanism of secondary emission and it is believed that this modification of the former method of measurement will increase the range of such investigations since the effects are larger and more easily measured.

56. Velocity distribution among thermionic electrons in vacuum and in hydrogen atmosphere. C. DEL ROSARIO, Yale University, (introduced by W. F. G. Swann).—The thermionic current from a tungsten filament to a coaxial cylindrical electrode was

measured for different retarding potentials first in vacuum and then in hydrogen, keeping the temperature of the filament constant. The heating current was made intermittent to eliminate potential drop along the filament when the thermionic current was being measured, and it's effective value was kept constant to 1/20 percent by a Wheatstone bridge arrangement of which the filament was made one arm. The filament temperature, determined from data of Forsythe and Worthing ranged from 1800°K to 1990°K, and the pressure of hydrogen was varied from 0 to 0.22 mm Hg. The distribution of velocities among the electrons was found to follow Maxwell's law, contrary to the experience of other observers, for a gas in thermal equilibrium with the filament for both vacuum and hydrogen atmosphere.

57. The adsorption of caesium on tungsten and oxidized tungsten. JOSEPH A. BECKER, Bell Telephone Laboratories, Inc.—By means of a method previously described it is possible to determine the number of caesium atoms and ions that evaporate from a cm^2 of tungsten at various temperatures when the tungsten is covered to various extents. The results are exhibited by curves showing rates of evaporation versus fraction of the surface covered. A typical isothermal rises sharply at the origin, reaches a maximum for 1 percent of covering, then decreases exponentially until the covering is 20 percent when it again rises steeply. The first rise and fall are due to ions, the second rise to atoms. These curves show that as more caesium is adsorbed ions evaporate less readily while atoms evaporate more readily. They explain (1) why positive ion emission versus temperature curves show a steep rise at an upper critical temperature at which the filament cleans off spontaneously, and a steep decline at a lower critical temperature; (2) the lack of discontinuities in the electron emission at these same temperatures; (3) why the filament may be covered to two different extents separated by a dividing edge; (4) why this edge travels along the filament; (5) how changes in the caesium vapor pressure affect these characteristics.

58. A new theory of ionic mobilities. A. P. ALEXEIEVSKY, University of California, (introduced by Leonard B. Loeb).—Recently, Loeb has shown in HCl gas that the ions are probably clusters of molecules about a charged molecule. Previous theories have accounted for the mobility of ions assuming that the clusters consist of but a few molecules. In this paper it is shown that it is possible to account for the mobility of these ions by assuming that the ion consists of a droplet of liquid HCl, condensation being caused by the electrical forces of the charged molecule. Assuming that the force of attraction between ion and molecule is given by $f=(D-1)e^2/2\pi Nr^5$ where D is the dielectric constant, e is the electron, N the number of molecules per cm^3 and r the distance of the HCl molecule from the charge, one can calculate from the expression $vdp=((D-1)e^2/2\pi r^5 N)dr$, using Van der Waal's equation, the radius R of the droplet which would be in equilibrium with any pressure of the gas. Placing the value of the radius so calculated in Epstein's equation for the mobility of a charged spherical droplet in an electrical field the mobility of the HCl ion is computed and found in good agreement with observed values. The equations also enables one to calculate the variation of the mobility with concentration in HCl air mixtures.

59. Molecular structure and the relative mobilities of positive and negative gaseous ions. LEONARD B. LOEB and A. M. CRAVATH, University of California.—Recently it has been shown by Loeb that the mobility of the negative ions in HCl gas is less than that of the positive ion. Condon made the suggestion that this was due to the presence of the H nucleus in the molecule which lay closer to the molecular surface than in most molecules. In a recent paper by Hund it is shown that both H_2O and H_2S exhibit the same general characteristics as HCl in the placing of the H nucleii. Mobility measurements have been made in these gases using the Franck modification of the Rutherford alternating current method. The mobilities of the positive ion in H_2S was 0.61 cm/sec per

volt/cm and that of the negative ion was 0.55 cm/sec per volt/cm. In water the mobilities were 0.62 and 0.56 cm/sec per volt/cm respectively. It is seen that these results are in agreement with the anticipation. The mobility values are relative to air, assuming 1.4 for positive and 1.8 for negative ions in cm/sec. per volt/cm.

60. Ether-drift experiments at Mount Wilson in February, 1926. DAYTON C. MILLER, Case School of Applied Science.—In February 1926, the ether-drift experiments were continued at Mount Wilson under very favorable conditions of weather. This series, consisting of 101 sets of observations involving 34000 readings, is the most extensive yet made for any one epoch. This epoch was chosen because, when combined with the epochs of 1925, it gives observations well distributed throughout the year. The new observations entirely confirm the results of the 1925 observations as announced at the Kansas City meeting. There is a periodic displacement of the interference fringes which is clearly systematic and cosmical in character; it is such as would be produced by a relative motion of the earth and the ether of 10 kilometers per second, the apparent apex of the earth's motion being a point in space having the right ascension of 255° and a north declination of 68°. The definitive values of the coördinates, from all available observations, are not yet determined. Causes for the observed phenomena other than relative motion are to be considered.

61. Faraday tubes and amperes rule. R. C. COLWELL, West Virginia University.—A new theory of Faraday tubes is outlined in which each tube is supposed to be made up of a succession of double doublets. These doublets have both electric and magnetic polarity. In a Faraday electric tube the electric poles are placed end to end and the magnetic poles are then perpendicular to the tube. In a Faraday magnetic tube, the electric poles are perpendicular to the tube. A Faraday tube always extends from a positive to a negative pole and shortens by an elision of the double doublets. When these doublets are elided they go out with a right hand twist thus giving rise to a closed electric or magnetic line of force. A lengthening of a Faraday tube reverses the direction of the closed magnetic (or electric) line of force. The single rule that "a shortening Faraday tube gives a right hand twist, a lengthening Faraday tube a left hand twist" is then sufficient to cover all cases of induced currents. It is also shown that this rule is equivalent to Ampere's rule regarding the attraction between two conductors which have currents in the same direction, so that Ampere's rule alone may be substituted for the many rules that are now given to determine the direction of an induced current.

62. The electric field of a charged wire and a slotted cylindrical conductor. CHESTER SNOW, Bureau of Standards.—The potential is found which is due to a fine wire (charged) in the presence of an outer shield at potential zero. This shield consists of a thin cylindrical shell, concentric with the wire, whose trace on a plane perpendicular to the latter consists of n equal, equally spaced circular arcs of a common circle. The problem is first simplified by a complex transformation $Z^n = z$, reducing it to that of a line charge in the presence of a single (incomplete) circular arc (a part of the circular arc $r = a$). This problem is solved for any position of the line charge, the solution being effected first by a transformation $z = a(i - z^1)/(i + z^1)$ which transforms the interior of this circle into the entire upper half of the z'-plane. The circular boundary then corresponds to the real axis of z'. This problem (that of a line charge in the presence of a finite straight line at zero potential) is again simplified by the transformation $z' = c \cos w$ which represents the entire z'-plane upon a semi-infinite strip in the w-plane. The proper (periodic) solution due to a line charge in this strip is then built up by an infinite series of images and their effect summed. By retracing the steps of the transformation, a solution in finite form is obtained for the original problem.

63. A new type of contact rectifier. L. O. GRONDAHL, Research Department, Union Switch and Signal Co.—A piece of copper with a layer of copper oxide formed on it at a high temperature is an unsymmetrical conductor of electricity. Ratios between high resistance and low resistance as high as 20,000 have been obtained. The unit consists of the oxidized piece of copper with a contact on the outer copper oxide surface made by means of a piece of lead or other soft metal applied under pressure. In a 1-1/2" disc, the low resistance may be a small fraction of an ohm and it is therefore capable of carrying comparatively high current. The capacity of such a disc is represented by a d.c. output of 5 watts. Cuprous oxide is an electronic conductor and the rectifier is therefore permanent. The effects of voltage and of pressure on resistance are similar to the corresponding effects in contact rectifiers, the principal difference being in the magnitude of the resistances. The voltage characteristic results in a very slight distortion of the rectified wave. No forming is necessary so the rectifier is immediately operative when the alternating voltage is applied. The units may be assembled like cells in a battery to supply higher voltages or greater currents.

64. Electrolytic conduction of potassium through glass. V. ZWORYKIN, Westinghouse Elec. & Mfg. Co., East Pittsburgh.—Burt has reported the successful introduction of sodium into a thermionic vacuum tube by electrolysis, the filament of the tube being connected to the negative terminal of a d.c. supply while the positive terminal is connected to a crucible containing molten sodium nitrate into which the tube is immersed. Attempts to duplicate the experiment with potassium were unsuccessful, the failure being attributed to the smaller mobility of potassium ions. The author has repeated Burt's experiments with different glasses and finds that for a soda potash glass immersed in KNO_3 the metal introduced into the tube is primarily sodium while the glass itself is enriched in potassium at the expense of sodium and becomes unusually brittle. When a potash glass, free from sodium, is used, potassium of high purity passes into the tube without corroding or embrittling the glass. This seems to show that Burt's negative results with potassium were due primarily to the difference in dimensions and molecular forces of potassium and sodium ions.

65. The sodium voltameter. ROBERT C. BURT, California Institute of Technology. —This voltameter, mentioned in recent publications, using the electrolysis of Na through glass, has been modified in form by using metal contact with the glass instead of thermionic emission. The voltameter not only possesses a large advantage over the silver voltameter because of the simplicity of the operation involved and reproducability under ordinary working conditions where the limit of refinement is not demanded, but it has also been shown to yield results which are certainly correct to 1 part in 2000, and probably to 1 part in 6000.

66. Contact electromotive force of carbon. BRIAN O'BRIEN, Buffalo Tuberculosis Association, Perrysburg, N. Y.—The carbon surface was prepared by depositing a thin layer of soot from pure benzol on a platinum ribbon. The contact e.m.f. was measured against cupric oxide by the Kelvin method with a precision of 0.01 volt. Freshly smoked surfaces in air before outgassing were positive to CuO by about 0.40 volt, with some variation between different surfaces prepared alike. Reduction of pressure from atmospheric to less than 10^{-6} mm mercury without heating made carbon slightly less electropositive, reaching a steady state. Outgassing carbon at successive temperatures up to 1400°C (the CuO at all times cool) made the carbon less electropositive, finally becoming negative to the CuO by 0.11 volt. The outgassing-contact e.m.f. curves were fairly reproducible on a number of surfaces. An outgassed surface allowed to stand in air became more electropositive, but did not return to initial value. There was no evidence of a final value characteristic of a completely denuded carbon surface, as further heating at higher temperatures rendered the carbon progressively more electronegative.

Effect of mercury vapor. Allowing mercury vapor at a pressure of 0.001 mm in the tube did not affect the contact potential difference between the carbon and the CuO.

67. Dielectric constant of an electrolyte. EDWARD M. LITTLE, University of Illinois, (introduced by Jakob Kunz).—Dielectric constant is related to electric moment per unit volume just as permeability is to intensity of magnetization. The electric moment of an electrolytic solution decreases with ionization, and the dielectric constant for 100% ionization of the solute equals that for the pure solvent (corrected for volume change). A critical value of dielectric constant, k_c, is assumed, above which the molecular binding forces in the solution are weakened sufficiently to allow all molecules to ionize. For values of k below this, thermal agitation together with the dielectric constant, occasionally ionizes a solute molecule. In general, for initial values of k less than k_c and also for some values greater, there is less than 100% ionization of the solute. A relation between n (ionized molecules per cc) and the concentration, c (molecules of solute per cc) is found, and as a relation between k, n, and c is known (because of the relation between k and intensity of electrification) the relation between k and c is then obtained. It is approximately a hyperbola. The initial drop in the experimental curves is due to grouping of molecules around ions, thus decreasing the intensity of electrification and therefore the dielectric constant.

68. Piezoelectric quartz oscillators coated with metallic films. E. O. HULBURT, Naval Research Laboratory, Washington, D.C.—Recent experiments have demonstrated that a quartz piezoelectric crystal with the sides coated with films of platinum, copper, or other metals, may be used in a suitable electron tube radio circuit as an *oscillator*, i.e. a *generator* of sustained current oscillations. Electrical connection was made to the metallic films by soldering small wires to the films or by a brush contact. The natural frequency of the crystal was changed but slightly by the addition of the metallic film. This frequency change with the weight of the film, the effect of the films on the other frequencies and harmonics, the effects of temperature, gas pressure, etc., are being investigated in detail. W. G. Cady has shown that a piezoelectric crystal coated with chemically deposited silver will serve as a resonator in a radio frequency circuit; its use as an oscillator, however, appears to have been unsuspected. In fact previous experience would suggest that a metallic film adhering to the crystal may destroy its oscillating properties, just as an oil film is known to do.

69. A new phenomenon dealing with the action of electrostatic fields upon electric currents. PALMER H. CRAIG, University of Cincinnati.—If the Hall effect is caused by a magnetic deflection of the free electrons within a metal, an analogous effect should be produced by an electrostatic field. An electrostatic potential of 17,000 volts was applied to the edges of a bismuth film 7.5×3.0 cms in area and 0.045 cms thick, by means of copper rods separated from the bismuth by sulphur or plate glass insulation. When a current of one ampere flowed through the strip longitudinally, a net transverse potential difference of about 40 microvolts was measured between point contacts at the edges midway between the ends of the film. This was a net effect after correction had been made for thermal effects, leakage currents and other causes masking the true effect. The transverse potential decreased with decreasing electrostatic field, longitudinal current and thickness of the film, and was measured by a potentiometer arrangement sensitive to 0.01 microvolt. Moving the point contacts towards the end of the strip also decreased the effect. No effect was observed in copper, silver and aluminum and it was therefore concluded that if the phenomenon exists in these metals it is of very much smaller magnitude than that in bismuth. The magnitude of the Hall effect is approximately 611 times that of the new effect when comparing the magnetic effect at 1000 gauss with the electrostatic effect at 17,000 volts, the same bismuth film and a longitudinal current of one ampere being employed in both cases.

70. Wave form of free electrical oscillations: self-capacity effect in multi-layer coils. ALLEN ASTIN, New York University. (Introduced by J. C. Hubbard).—Observations have been made of the wave form of the free oscillations of a section, or sections of a multilayer coil by itself, and with added capacities, using the drop chronograph method developed by J. C. Hubbard (Phys. Rev., **9**, 529, (1917)). From the results periods, self capacities and damping factors of the coil are determined. Periods are determined to less than 1/10 per cent. The resistance is determined from the decrement. From a calibration of the contacts of the instrument, using a constant potential, the oscillation potentials are found to be in excellent agreement with those calculated from the constants of the circuits. With a coil of rectangular cross section of winding, with layer windings in several sections, but with the unused sections disconnected, the free periods are approximately independent of the number of sections used.

71. The inductance of a helix made with wire of any section. CHESTER SNOW, Bureau of Standards.—A formula has been derived for the inductance of a single layer helix which is to be used in absolute measurements of precision. It takes account of the helical nature of the winding and hence of the axial component of current in it. It is derived for any shape of wire section and is especially simple if this is symmetrical about each of two axes passing through its center of gravity. It is correct to the second order inclusive in small quantities like the ratio of the dimensions of the wire section to the radius of the cylindrical form. The current density is not assumed to be uniform but the formula applies (to the second order) to any current distribution which is developable by Maclaurin's theorem over the section of the wire. The formula is specialized and simplified for the cases of wires having circular or rectangular section. For windings of ordinary dimensions a precision is claimed of at least one part in a million.

72. The resistance of condensers at radio frequency. R. R. RAMSEY, Indiana University.—The condenser was placed in a "differential thermometer" made of two 800 cc pyrex glass beakers inverted on and sealed to two glass plates. Through each glass plate three holes were drilled. In two of these, electrical connections were placed and through the third a glass tube was sealed. To the glass tubes was fastened a U-tube filled with water. The height of the water in the tubes served to indicate the relative pressure in the two beakers. The radio condenser, which was an eleven plate variable condenser of "low loss" construction, was placed in one of the beakers and connected to the electrical connections which extended through the glass plate. In the second beaker a second condenser exactly like the first was placed, but this condenser was not connected to the terminals. A short piece of resistance wire was connected to the electrical terminals. The first condenser was connected into a radio frequency circuit and the resistance wire was connected to the electrical terminals. The first condenser was connected into a radio frequency circuit and the resistance wire was connected to a D.C. circuit. Then assuming that both beakers are exactly alike thermally when the pressures as indicated by the water in the U-tube are the same, we have I^2R in the high frequency side is equal to i^2r in the D.C. side. The average of a number of determinations at a frequency of 10^6 cycles, was .098 ohms. The individual results varied from .05 ohms to .15 ohms, the condenser being set so that the capacity was .00008 microfarads.

73. Establishment of radio standards of frequency by the use of a harmonic amplifier. C. B. JOLLIFFE and GRACE HAZEN, Bureau of Standards.—One method used by the Bureau of Standards in establishing radio standards of frequency consists in the "stepping up" from a known standard audio frequency to a radio frequency by the use of harmonics. The low-frequency output is carried through an amplifier arranged to distort and so produce harmonics. By means of tuned circuits a harmonic is selected which in turn serves as a fundamental for further distortion and amplification to give the desired frequency with sufficient power to operate the frequency meter under standardization.

A fixed radio-frequency generator such as a piezo oscillator, or a fixed audio-frequency generator such as an electric-driven tuning fork, can likewise be standardized by the use of the harmonic amplifier with the addition of a sonometer for measuring an audio-frequency beat note produced by a harmonic from the standard audio-frequency source and the fundamental or harmonic from the fixed-frequency generator. The frequency of the beat note is impressed on the steel wire of the sonometer by means of a telephone receiver magnet. The vibration frequency of the wire is calculated by means of the constants of the wire and the tension applied.

74. Cooperative investigation of radio fading. J. H. DELLINGER, C. B. JOLLIFFE and T. PARKINSON, Bureau of Standards.—Signal intensity fluctuation is one of the chief barriers to reliable long distance reception of broadcasting and of the higher radio frequencies. With a view to securing quantitative data on this phenomenon the Bureau of Standards invited a number of university and other laboratories to engage in a co-operative program of fading measurements. This report summarizes the progress made in 1925 when five series of simultaneous observations were made on certain specially arranged transmissions from broadcasting stations. Twenty laboratories in the eastern half of the United States were engaged in the work. The measurements consisted of recording graphically variations of deflection of a galvanometer connected to radio receiving apparatus so as to indicate directly variations in the received field intensity. These records were supplemented in some cases by absolute measurement of the field intensity and by simultaneous continuous records of direction variation. The measurements yielded data of value on the characteristic radio wave phenomena during a solar eclipse, during the sunset period and the variations throughout the whole diurnal cycle.

75. Reception currents from a loop antenna. R. C. COLWELL, West Virginia University.—If the oscillations in the four sides of a loop antenna are regarded as made up of the oscillations of a succession of vibrating doublets, an integration around the the loop will give the resultant electric vector for any point in space. For the two vertical sides of the loop, the electric intensity takes the form $E_\theta = (2I \tan \theta/cr_0)(1-\cos 2\pi h \cos \theta/\lambda r_0)^{\frac{1}{2}}(1-\cos 2\pi aX/\lambda r_0)^{\frac{1}{2}}$ This equation shows that a loop has a directional effect high up in the air as well as along the ground. If the integration is taken over one vertical and one horizontal side, we have the electric intensity due to a bent antenna. The resulting equation is in the form

$$E_\theta' = (Ic/r_0)\ ((A+B\cos\alpha)^2+(C+D\cos\alpha)^2)^{\frac{1}{2}}$$

The cos α changes sign when the azimuth is 90° in such a way as to give a directive effect to the wave sent out from this antenna; the intensity being greatest for azimuth 180° and least for azimuth 0°.

76. A ballistic galvanometer as an integrating instrument. H. L. CURTIS and C. MOON, Bureau of Standards.—The formula for the capacitance when using Maxwell's absolute bridge is derived assuming that the time integral of the current through the galvanometer is zero. This paper shows the conditions which must be fulfilled by a galvanometer in order that it will correctly integrate the current. With all integrating galvanometers the torque produced by the current through the coil shall at every instant be proportional to this current. This will be the case only if the coil is non-magnetic and if the current through the coil does not affect the field of the permanent magnet. This last condition can be experimentally realized by finding the position of the coil where the reversal of the applied electromotive force does not change the galvanometer reading. A second requirement applies only to conditions similar to those in a Maxwell bridge. These conditions are such that the curve of motion of the galvanometer coil as a function of time is a series of parabolas. In order that the time integral of current shall be zero, the time integral of deflection must also be zero. This requires that the

excursions shall be on both sides of the galvanometer zero, but not an equal amount on the two sides. The ratio on the two sides is as two to one.

77. Magnetostriction in permalloy. L. W. McKeehan and P. P. Cioffi, Bell Telephone Laboratories, Inc.—The specimens examined were well-annealed 1 mm wires, 40 cm long, of iron, nickel, and permalloys containing from 46 to 89 percent nickel. Changes in the magnetization were measured ballistically. Changes in the length of part of the specimen were multiplied two million times by a mechanical lever, an optical lever, a multiple slit, a photo-electric cell and a sensitive galvanometer. Measurements were made with or without tension. The rate of increase in magnetostriction with magnetization, at zero magnetization, was zero in all cases. Permalloys with less than 81 percent nickel expanded, those with more than 81 percent nickel contracted when magnetized. Tension reduced the expansions and increased the contractions. The theory of atomic magnetostriction (Phys. Rev. **26**, 274, (1925)), explains the new results and suggests that orientation of the magnetic axes of iron and nickel atoms, precisely like that due to the application of magnetic fields, may be effected by mechanical stresses within the elastic limit. Changes in electrical resistance (Phys. Rev. **23**, 114, (1924)) support this view.

78. Hall effect in mono-crystalline copper. P. I. Wold, Union College.—The Hall effect has been measured in a single crystal of copper in the form of a rod 15 cm long and .55 cm in diameter. The crystal was cubic with an axis nearly coincident with the longitudinal axis of the rod. Transverse contacts were obtained by copper terminals spring pressed against the sides of the rod, the rod being placed in a holder which permitted rotation about the longitudinal axis. The Hall constant varied with rotation, but only by relatively small quantities which were irregular and apparently due to difficulty in maintaining stable transverse contact. If the Hall constant parallel to an edge of the crystal cube is R_1 and that at right angles thereto is R_2, the results are in agreement with the relation that in intermediate directions the resultant constant is $R = R_1 \cos^2 x + R_2 \sin^2 x$. In the case of a cubic crystal $R_1 = R_2$.

79. The effect of small amounts of silicon on the thermo-magnetic change point "*A2*" in mild steel. F. C. Farnham, New York University (Introduced by H. H. Sheldon).—Tests have been made on samples of steel containing .25 percent carbon with varying silicon content up to 3 percent. It is observed that for small amounts of silicon, up to about .5 percent, the point "A2" is lowered rather rapidly; for added amounts, up to about 2 percent, the lowering of "A2" is much less; and for amounts between 2 percent and 3 percent the rate of lowering of "A2" is again greater. From these results it is evident that the presence of the carbon greatly modifies the effect of silicon as observed in ferro-silicon alloys.

80. Magnetic moments of the alkali metal atoms. John B. Taylor, University of Illinois, (introduced by W. H. Rodebush).—The results previously reported on sodium (Kansas City meeting) have been confirmed, showing that the neutral sodium atom possesses a moment closely equal to one Bohr magneton. Potassium has also been investigated and shows, likewise, the single magneton value.

The amounts of deflection or splitting of the atomic rays of sodium and potassium are related inversely as the temperatures of evaporation, in accord with the equations for the effect. Distinct images of the divided rays have been obtained.

81. The Zeeman effect, the Stern-Gerlach experiment and the magneton. Jakob Kunz, University of Illinois.—Landé and Sommerfeld have given a classification of the anomalous Zeeman effect, which makes it possible to determine the number of magnetons in an atom if the multiplicity, the ground term of the atom and the inner quantum

number are given. These numbers have been supplied to the writer by P. D. Foote for most of the elements. The number of "lines" to be expected in the Stern-Gerlach experiment, and the number of Bohr magnetons has been calculated. It has been shown moreover that especially for the rare earth elements the agreement between these calculations and recent measurements is satisfactory.

82. Direct absolute measurement of acoustic impedance. G. W. STEWART, University of Iowa.—Advantage is taken of the author's theory of the transmission in an acoustic line with an attached branch which alters the intensity and the pressure phase of the transmitted sound. By the measurement of the relative intensities and phases with and without the branch present, it is possible to obtain the components Z_1 and Z_2 of the impedance, $Z=Z_1+iZ_2$, of the branch. If S is the area of the conduit, P_0 and P_0' the two pressure amplitudes, ϵ the change in phase, ρ the density of the medium, a the velocity of sound therein, $Z_1=(\rho a/2S)\ [A/(A^2+B^2)]$ and $Z_2=(\rho a/2S)\ [B/(A^2+B^2)]$, wherein $A=(P_0/P_0')\cos\epsilon-1$ and $B=-(P_0/P_0)\sin\epsilon$. The method involves only the *relative* magnitudes of pressure amplitudes and the direct measurement of phase change, the knowledge of density and velocity being sufficiently accurate. In the present application the pressure ratio is determined by altering a comparison source, and the phase is measured directly. The method involves only one simple absolute measurement and is a strictly acoustic method somewhat analogous to methods of measurement long used in electricity.

83. Effect of amplitude on the frequency of a tuning fork. C. MOON and H. L. CURTIS, Bureau of Standards.—There has been devised a method for the precise rating of a tuning fork by comparison with a pendulum. A series of flashes of twice the fork frequency are obtained by means of slits in a pair of vanes carried by the prongs of the fork giving images on a moving film, formed by two concave mirrors, one attached to the pendulum and the other to the pendulum support. The frequency of the fork is computed from the trace on the film. An accuracy of five parts in a hundred thousand can be obtained from the record over a single second of time. Two 100 cycle forks, one of steel, the other of elinvar were studied. When vibrating freely showed nearly a linear increase in frequency with decreasing amplitude. The elinvar fork increased ten parts the steel fork three parts in a hundred thousand as the amplitude decreased from 1.0 mm to 0.25 mm. With either of the forks maintained at a constant amplitude by a vacuum tube drive, the frequency could be changed by a part in ten thousand by varying the condiions in the tube circuits. Hence there can be no proper discussion of the effect of amplitude on the frequency of a driven fork.

84. Hysteresis due to the Ewing effect in the flexure of bars. G. H. KEULEGAN, Bureau of Standards, (introduced by L. J. Briggs).—Boltzmann's theory of elastic time effects does not always account for the entire hysteresis observed in the deformation of an elastic body during a closed load cycle. The author, therefore, has made an attempt to formulate an additional theory of hysteresis which is independent of time effects and calls such hysteresis the "Ewing effect." The basis of the theory is the assumption that the stress-strain curve of an elastic body, instead of being a straight line, consists of a symmetrical loop. The deductions from the theory as applied to the flexure of bars are as follows: (a) In the flexure of bars the energy lost owing to the "Ewing effect" varies with the third power of the maximum load of the load cycle and with the fourth power of the length of the bar. (b) The distribution of hysteresis is parabolic and is independent of the maximum load and of the length of the bar. Again, a general deduction from the theory is that the loss of energy per unit volume for a tensional stress range σm is $1/3\beta\sigma_m{}^3$. Experiments gave $\beta=1.33\times10^{-6}$ ergs cm^3 per kg^2 for Armco iron; so that energy loss per cubic centimeter due to hysteresis is 26,000 ergs for a stress range of 3900 kgs per cm^2.

85. The expansion of copper from absolute zero to the melting-point. THOMAS A. WILSON and WHEELER P. DAVEY, General Electric Company.—Copper bars of rectangular cross-section, 3/8 inch on a side and approximately 30 cm long, were supported on powdered alumina in an alundum tube wound with a molybdenum heating coil lagged with a wrapping of asbestos $2\frac{1}{2}$ inches thick. The tube extended 2 inches beyond each end of the copper so minimizing end cooling. Two holes 3/8 inch square drilled through the tube and asbestos permitted reading the position of the ends of the copper with a horizontal cathetometer. The experiments were conducted in a hydrogen atmosphere. The power through the heating coil was increased approximately 100 watts every 24 hours, at the end of which period a reading was made. At temperatures near the melting-point, readings were made quite frequently. Two experiments gave the linear expansion of copper per cm length from room temperature (27°C) to the melting-point as .0257 cm and .0264 cm . With data from Landolt-Bornstein, the calculated expansion from absolute zero to 27°C is .0034 cm per cm length, making the total expansion from absolute zero to the melting-point .029[1] cm per cm length.

86. The expansion of crystals from absolute zero to the melting point. WHEELER P. DAVEY, General Electric Company.—In a face-centered cubic crystal each atom lies in a "pocket" formed by three adjacent atoms of a 1 1 1 plane (the slip plane) so that the four atoms form a tetrahedron. At 0°K the "atomic domains" are assumed to be in contact. It seems plausible that, in such a crystal 12½ percent of the tetrahedra must expand 4½ percent along each edge before all the surface atoms can leave the solid. But at any instant 12½ percent of the tetrahedra are 1.7 times the most probable size. A linear expansion of 2.6 percent from 0°K is therefore a prerequisite to melting for a face-centered cubic crystal. Added to this will be the expansion occurring while the atoms take up additional energy to overcome cohesion. Expansions calculated from the literature are Al 2.4 percent; Mg (having an analogous structure), 2.4 percent; Ag 2.3 percent; Cu 2.4 percent; Ni 2.9 percent. These are probably all low because of extrapolations. Recent measurements of Cu (see previous abstract) indicate 2.9 percent. Body-centered cubic crystals require no expansion except what occurs while overcoming cohesion. Na and K become non-crystalline before melting. W expands 2 percent corresponding to its high interatomic attraction.

87. Thermal properties of butane, isobutane, propane, and ethane. LEO I. DANA, Linde Air Products Company, Buffalo, N. Y.—The investigation is intended to cover the thermal properties of these liquids in the saturation region over the range of pressures and temperatures required for the use of these gases as refrigerants. The latent heats of vaporization and the specific heats of the liquids of ethane and propane have been determined from −40°C to +30°C; of isobutane and butane from −13°C to +30°C. An aneroid calorimeter, enclosed by a vacuum jacket, operating adiabatically and thus avoiding heat leak corrections, was employed. The vapor pressures of the first three have been measured from one half atmosphere absolute to about 6 atm. abs. and the measurements are being extended to higher pressures. The liquid and vapor densities of the first three gases have been measured from 0°C to 60°C. New forms of cryostats have been constructed for the low temperature measurements.

88. Thermal conductivity of lithium, sodium and lead to −250°C. CHARLES C. BIDWELL, Cornell University.—The bar method of Forbes was modified as follows. The metal rod, centered in a large test tube, was placed in a constant temperature bath and heated by a coil at the upper end. Air convection in the tube was stopped by cardboard disks through which the rod was threaded and which were spaced at short intervals along the rod. Temperature gradient was determined by thermojunctions spaced along the rod. Cooling curves were obtained on smaller lengths of the rod similarly mounted. With mean temperature not exceeding 15° above bath temperature accurate values of

k were obtained. Values for lead from -250°C to $+100$°C taken to test the method agreed well with the best recorded values. Lithium shows a linear increase in k from 0.15 at 0°C to 0.20 at -200°C, thereafter rising sharply to 1.00 at -246°C. Above 0°C a minimum occurs at $+40$°C and an increase thereafter to 0.17 at $+140$°C. Sodium shows a linear increase from 0.28 at -40°C to 0.40 at -240°C. Above -40°C an increase occurs to 0.35 at 0°C and thereafter a decrease to 0.28 at $+65$°C. The breaks in these lines correspond to breaks previously reported in electrical conductivity and thermo-electric power lines for these metals.

89. Thermal conductivity of metals at high temperatures. M. F. ANGELL, University of Idaho.—This paper describes a continuation of former work with improved methods. The metal is heated electrically in the form of a long hollow cylinder. In the earlier experiments the heat flow was assumed to be radial at a point midway between ends, but in these experiments this assumption is made for the point of maximum temperature along the cylinder. The thermal conductivity is calculated from the temperature gradient along the radius at this point and from the energy transmitted. Complete curves of the thermal conductivity from 50°C to the melting point are given for copper, zinc and lead. For copper the thermal conductivity was found to be .92 at 50°C, decreasing very slowly to .90 at 500°C, then more rapidly to .8 at 1000°C. The conductivity of zinc decreases from .265 at 50°C to .215 at 400°C. The conductivity of lead decreases from .082 at 50°C.

90. The ratio of heat losses by conduction and by evaporation from any water surface. I. S. BOWEN, California Institute of Technology.—From theoretical considerations it is shown that the process of evaporation and diffusion of water vapor from any water surface into the body of air above it is exactly similar to that of the conduction or "diffusion" of specific heat energy from the water surface into the same body of air. Due to this similarity it is possible to represent the ratio R of the heat loss by conduction to that by evaporation by the formula, $R=.46(T_w-T_a)P/(P_w-P_a)760$, where T_a and P_a are the original temperature and vapor pressure of the air passing over the lake, and T_w and P_w are the corresponding quantities for the layer of air in contact with the water surface. The substitution of R times the evaporation loss for the value of the conduction heat loss in the Cummings equation for evaporation makes it an exact equation for the determination of evaporation from any water surface in terms of the net radiant energy absorbed by the water and the heat stored in the water.

91. Surface tension of sodium. F. E. POINDEXTER, Washington University.—The surface tension of sodium was determined in a high vacuum at a series of temperatures ranging from 105°C to 245°C. A modified flat drop method was used. The values taken from the best mean straight line through the experimental points gave the values of 222 dynes per cm at 100°C and 211 at 250°C. This gives a temperature gradient of .072 dynes per degree. From the Eotvos relation $\gamma v^{2/3}=k(T_0-T)$ we get upon differentiating with respect to T, $v^{2/3}d\gamma/dT=-k$, where γ is the surface tension, v is the volume of a gram atom, T is the temperature and T_0 and k are constants. Taking the density of sodium as .91 at 100°C, we find $v=8.6$. This together with the experimental value of .072 for $d\gamma/dT$ gives us $k=.62$. This is taken to mean that the molecules in liquid sodium are polyatomic, since the value of k for non-associated liquids is 2.2.

92. Pressure distribution over airfoils at high speeds. L. J. BRIGGS and H. L. DRYDEN, Bureau of Standards.—The forces exerted on a body by an airstream of speed not greater than a few hundred feet per second depend on the airspeed, V, size of the body as given by a linear dimension, L, air density, ρ, and viscosity, μ, in the manner described by the equation

$$\text{Force}/(\tfrac{1}{2}\rho V^2L^2)=\phi(VL\rho/\mu).$$

At high speeds the influence of the compressibility of the air becomes appreciable and the force coefficient is a function of the ratio of the air speed to the speed of sound as well as of the Reynolds number, $VL\rho/\mu$. The variation of force coefficient with Reynolds number is small whereas the variation with speed ratio has been found by the authors, together with G. F. Hull, to be large. The work now described gives a more extensive and systematic series of observations on airfoil sections of 1 inch chord including observations of flow near the surface. The large changes in forces were found associated with a breaking away of the flow from the surface. The pressure distribution furnishes data to the propeller designer regarding the load distribution encountered at high speeds. The paper will be published as a Technical Report of the National Advisory Committee for Aeronautics.

93. Compensation of altimeters and altigraphs for air temperature. W. G. BROMBACHER, Bureau of Standards.—The altitudes of aircraft are usually determined by an altimeter, which is an aneroid barometer calibrated to an altitude-pressure relation containing an arbitrary altitude-temperature assumption. For the accuracy required in aeronautics, altitudes should be determined by both pressure and temperature measurements. It is difficult to take account of the mean temperature term of the barometric formula mechanically in an instrument. The following new relation based on the summer, winter, and yearly averages of observations of upper air temperatures at latitude 40° in the United States is presented as a substitute. Up to 30,000 feet: $dP/dt = A_h$, (1) where P is the pressure and T the absolute temperature at the altitude h, and A_h is a constant for any one altitude. Further, values of A_h give values of K varying from 0.0023 to 0.0038 in the following important relation for instrument work, $A_h/(P_0 - P) = K$, (2) where P_0 equals 760 millimeters of mercury pressure. Altitudes according to relations (1) and (2) can be indicated by using a temperature element ("air temperature compensation") or a manually operated device to modify the multiplication of the mechanism ("ground temperature compensation"). The manually operated device modifies the multiplication according to an average value of K and the temperature dial is graduated in terms of ground level temperatures.

94. The effect of a high temperature in disrupting ice. HOWARD T. BARNES, McGill University.—Our knowledge of the mode of transfer of heat across very steep temperature gradients is practically nil. The author has been experimenting in this field by driving a powerful energy charge into solid ice cooled below the freezing point. An intense exothermic reaction is rapidly generated by burning a mass of aluminum and the temperature is raised in 5 to 8 seconds to 2500°C. The disruption of the ice below 0°C is observed. Ice is, in this way, converted into a high explosive, the atoms being driven out of the molecules without melting the ice. In large masses a slow explosion occurs which resembles the reaction of black powder set off at a low temperature rather than the sudden detonation of dynamite. Ordinary welding thermit has been used conveniently, since that material is not in itself explosive. Application of this method has been made practically, as it offers a powerful means for relieving ice accumulations.

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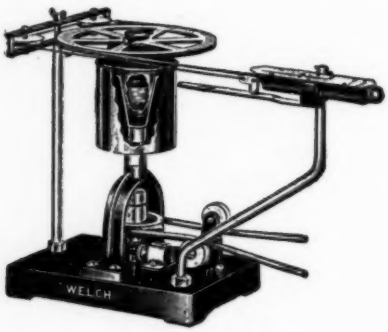

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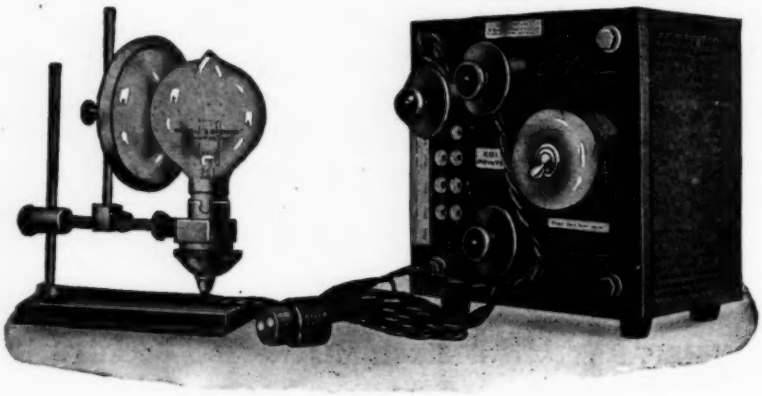

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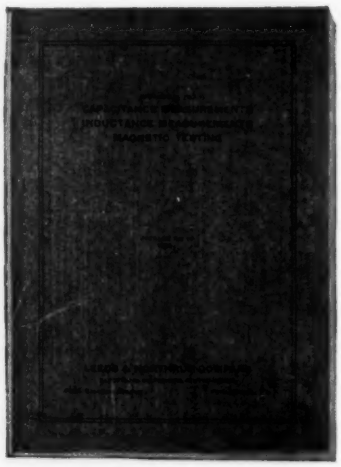

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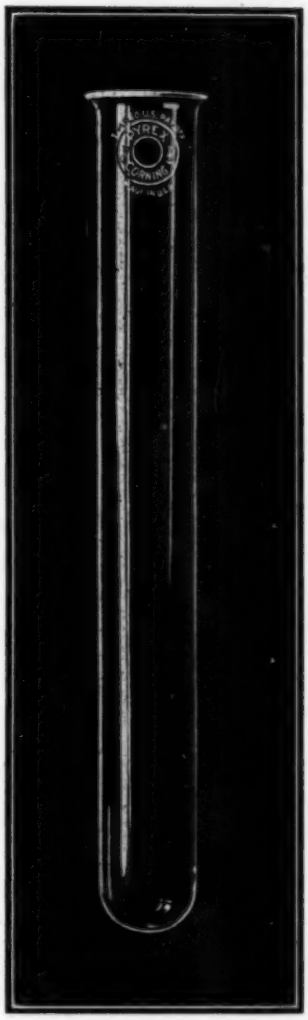

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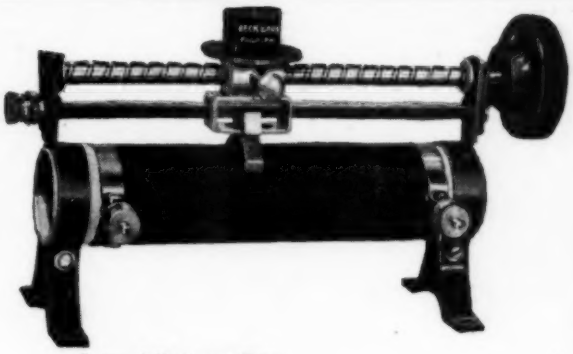

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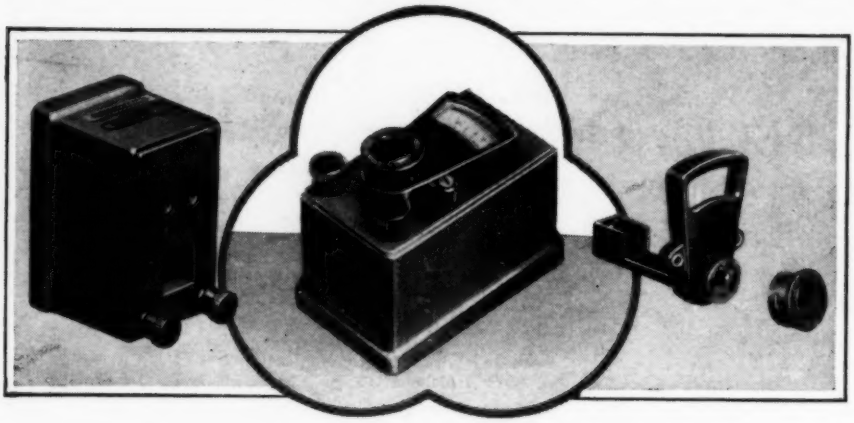

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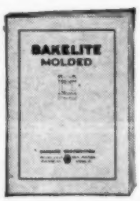

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